Preparation of Coordinatively Asymmetrical Ruthenium(II) Polypyridine Complexes

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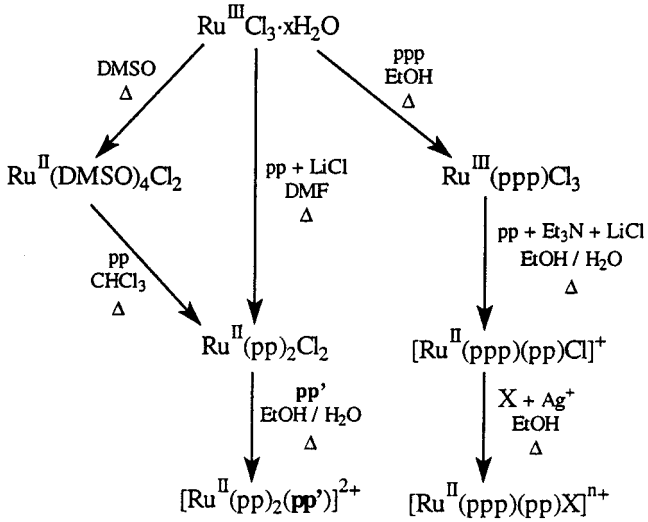
A series of salts of the type *cis*-$[Ru^{II}(bpy')(bpy'')(CO)_2](PF_6)_2$ (bpy′ and bpy″ represent different bipyridine derivatives) have been prepared by using literature procedures and utilized as precursors for the preparation of highly functionalized complexes of Ru^{II} incorporating neutral and anionic, mono- and bidentate, nitrogen-, phosphorus-, sulfur-, and oxygen-donor ligands. The new synthetic approach builds upon previous work with the trimethylamine *N*-oxide-assisted removal of the carbonyl ligand. Difficulties with the use of this potent oxidant in the presence of reducing ligands such as dppe and nitrite have been overcome by the use of acetonitrile complexes of the type *cis*-$[Ru(bpy')(bpy'')(CH_3CN)_2]^{2+}$ and pyridine complexes of the type *cis*-$[Ru(bpy')(bpy'')(py)_2]^{2+}$ as highly versatile intermediates. Strategies for the selective removal of a single carbonyl ligand from the precursors have been developed and used to synthesize the highly asymmetrical complexes *cis*-$[Ru^{II}(bpy')(bpy'')(py)(CO)]^{2+}$ and *cis*-$[Ru^{II}(bpy')(bpy'')(py)(NO)]^{3+}$. The synthetic chemistry has been extended by using either of these complexes and the complex-as-ligand strategy to prepare the pyrazine-bridged complex *cis*,*cis*-$[(Ru^{II}(bpy')(bpy'')(py))_2(pz)](PF_6)_4$ (pz is pyrazine). Finally, a methodology for the preparation of isothiocyanate complexes such as *cis*-$Ru(bpy')(bpy'')(NCS)_2$ has been developed. For the pyridyl/carbonyl, pyridyl/nitrosyl, and ligand-bridged complexes, geometrical isomers were formed in statistical yields. For the isothiocyanate complex *cis*-$Ru(dmb)(4,4'-(COOEt)_2bpy)(NCS)_2$, the majority (N,N-bound) isomer was isolated from the other three linkage isomers. For all the syntheses reported, yields were high, 44−96%, and each procedure appears to be both general and redundant in that multiple schemes are possible for the preparation of most targets.

Introduction

More than 7000 manuscripts involving polypyridyl complexes of ruthenium(II) have been published, most of them in recent years. This interest has been sustained in no small part due to the relatively straightforward synthetic chemistry developed previously. The products of these syntheses along with polypyridyl complexes of rhenium(I) and osmium(II) have been used in chromophore-quencher assemblies,[1−12] as new dyes for use as sensitizers[13−17] and as chemiluminescent and electrochemiluminescent materials.[18,19] Even with this progress, the underlying chemistry has relied on a handful of synthetic approaches.

Scheme 1[a]



[a] pp and pp′ are bidentate pyridyl ligands and ppp is a terdentate pyridyl ligand.

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(1) Boyde, S.; Strouse, G. F.; Jones, W. E.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7448.
(2) Jones, W. E.; Bignozzi, C. A.; Chen, P.; Meyer, T. J. *Inorg. Chem.* **1993**, *32*, 1167.
(3) Fox, M. A.; Chanon, M. *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Vol. D.
(4) Indelli, M. T.; Scandola, F.; Flamigni, L.; Collin, J. P.; Sauvage, J. P.; Sour, A. *Inorg. Chem.* **1997**, *36*, 4247.
(5) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: New York, 1991.
(6) Scandola, F.; Bignozzi, C. A.; Indelli, M. T. *Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds*; Kluwer Academic: Dordrecht, The Netherlands, 1993.
(7) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163.
(8) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193.
(9) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.
(10) Petersen, J. D.; Murphy, W. R.; Sahai, R.; Brewer, K. J.; Ruminski, R. R. *Coord. Chem. Rev.* **1985**, *64*, 261.
(11) Creutz, C.; Chou, M.; Netzel, T. L.; Okunura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309.
(12) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717.
(13) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.
(14) Anderson, P. A.; Strouse, G. F.; Treadway, J. A.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 3863.
(15) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Muller, P.; Liska, N.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.
(16) Castellano, F. N.; Heimer, T. A.; Tandhasetti, T.; Meyer, G. J. *Chem. Mater.* **1994**, *6*, 1041.
(17) Brauns, E.; Jones, S. W.; Clark, J. A.; Molnar, S. M.; Kawanishi, Y.; Brewer, K. J. *Inorg. Chem.* **1997**, *36*, 2861.

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This is even true for the preparation of composite materials such as ruthenium(II)-derivatized polymers,[20−24] peptides and proteins,[25−29] modified surfaces,[30−32] and supramolecular assemblies.[33]

The most common synthetic approach to the preparation of mixed-chelate complexes is depicted in Scheme 1. $Ru^{III}Cl_3 \cdot xH_2O$ is used as a starting material for the preparation of $Ru(pp)_2Cl_2$, pp being a polypyridyl or derivatized polypyridyl ligand.[18,34−36] With thermally sensitive ligands, $Ru^{II}(DMSO)_4Cl_2$ (DMSO is dimethyl sulfoxide) has been used as a synthetic intermediate.[37−41] As shown in Scheme 1, a related procedure has been utilized for preparation of complexes containing terdentate ligands such as terpyridine.[42−47]

The principal limitation of these approaches is the necessity that two of the polypyridyl ligands be the same. Attempts have been made previously to prepare tris(heteroleptic) complexes, mixed-chelate complexes incorporating three different bipyridyl ligands, but they have been met with only limited success.[48−51] Recently, a procedure was published which presented a general method for the synthesis of tris(heteroleptic) complexes of the form $[Ru^{II}(bpy')(bpy'')(bpy''')]^{2+}$ in which bpy′, bpy″, and bpy‴ represent three different bipyridyl ligands.[52−54] Examples of ligands used are shown in Figure 1 and the method is summarized in Scheme 2. Briefly, the first bipyridyl ligand is inserted into the μ-dichloro bridge of oligomeric *cis,cis*-$[Ru^{II}(CO)_2Cl_2]_n$ to prepare *trans(Cl),cis(CO)*-$Ru^{II}(bpy')(CO)_2Cl_2$, which is subsequently converted to the triflato complex *cis,cis*-$Ru^{II}(bpy')(CO)_2(CF_3SO_3)_2$. Addition of a second bipyridyl ligand yields *cis*-$[Ru^{II}(bpy')(bpy'')(CO)_2]^{2+}$, which can be oxidatively decarbonylated with trimethylamine *N*-oxide by conversion of the CO ligand to CO_2. Carrying out the decarbonylation in the presence of a third bipyridyl ligand yields the final product, $[Ru^{II}(bpy')(bpy'')(bpy''')]^{2+}$. The use of this procedure has led to the successful preparation of over 50 new compounds.

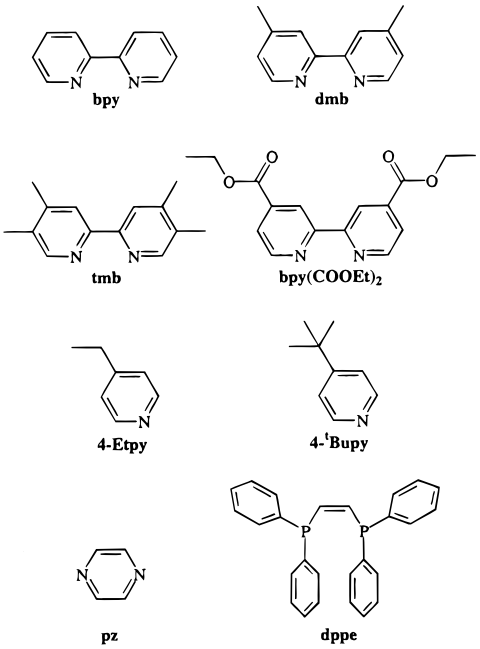
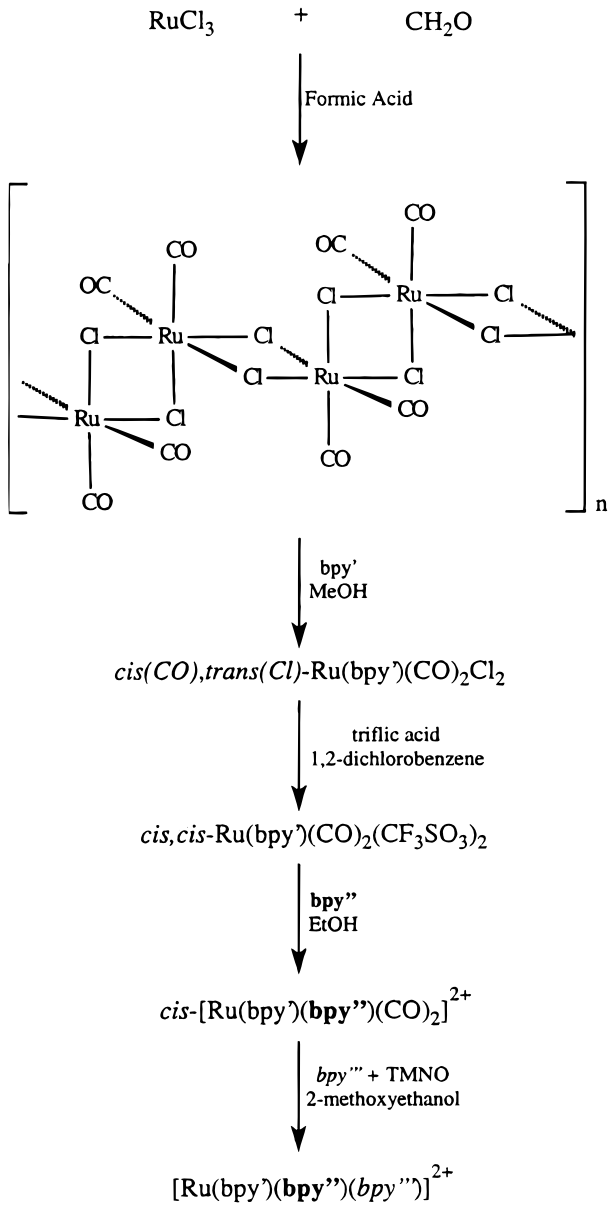


Figure 1. Ligand structures. bpy = 2,2′-bipyridine; dmb = 4,4′-dimethyl-2,2′-bipyridine; tmb = 4,4′,5,5′-tetramethyl-2,2′-bipyridine; 4,4′-$(COOEt)_2$bpy = 2,2′-bipyridine-4,4′-dicarboxylic acid, diethyl ester; 4-Etpy = 4-ethylpyridine; 4-^{t}Bupy = 4-*tert*-butylpyridine; pz = pyrazine; dppe = bis(diphenylphosphinoethylene).

This method, too, has its limitations. For instance, it is difficult to add acid-sensitive ligands in the first step because the replacement of the chloro ligands with triflato ligands is best carried out in the presence of excess triflic acid. Generally (although not always), this limitation can be avoided by altering the order in which ligands are added to the complex or by using a significantly lower yield method involving Ag^+-assisted removal of the chloro ligand at neutral pH. A greater limitation is the requirement that all ligands be bidentate. In addition, trimethylamine *N*-oxide, used for decarbonylation, is highly reactive and ligands that are easily oxidized cannot be used. These include nitrites and phosphines among others. Also, the method does not allow for the incorporation of ligands other than pyridines and there is not access to halides, pseudo-halides, oxygen donors, sulfur donors, phosphorus donors, and others as ligands.

(18) Juris, A.; Barigelletti, S.; Campagna, S.; Balzani, V.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
(19) Tokel-Takvoryan, N. E.; Hemingway, R. E.; Bard, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 6582.
(20) Younathan, J. N.; Jones, W. E.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 488.
(21) Jones, W. E.; Baxter, S. M.; Strouse, G. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 7363.
(22) Baxter, S. M.; Jones, W. E.; Danielson, E.; Worl, L. A.; Strouse, G. F.; Younathan, J.; Meyer, T. J. *Coord. Chem. Rev.* **1991**, *111*, 47.
(23) Rasmussen, S. C.; Thompson, D. W.; Singh, V.; Petersen, J. D. *Inorg. Chem.* **1996**, *35*, 3449.
(24) Margerum, L. D.; Meyer, T. J.; Murray, R. W. *J. Phys. Chem.* **1986**, *90*, 2696.
(25) Mecklenburg, S. L.; McCafferty, D. G.; Schoonover, J. R.; Peek, B. M.; Erickson, B. W.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 2974.
(26) Mecklenburg, S. L.; Peek, B. M.; Schoonover, J. R.; McCafferty, D. G.; Wall, C. G.; Erickson, B. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 5479.
(27) Mecklenburg, S. L.; Peek, B. M.; Erickson, B. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 8540.
(28) Wright, J. L.; Wang, K.; Geren, L.; Saunders, A. J.; Pielak, G. J.; Durham, B.; Millett, F. *Adv. Chem. Ser.* **1998**, *254*, 99.
(29) Hamachi, I.; Tanaka, S.; Tsukiji, S.; Shinkai, S.; Oish, S. *Inorg. Chem.* **1998**, *37*, 4380.
(30) Moss, J. A.; Argazzi, R.; Bignozzi, C. A.; Meyer, T. J. *Inorg. Chem.* **1997**, *36*, 762.
(31) Leasure, R. M.; Moss, J. A.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 1247.
(32) Dalton, E. F.; Murray, R. W. *J. Phys. Chem.* **1991**, *95*, 6383.
(33) Yang, J.; Seneviratne, D.; Arbatin, G.; Andersson, A. M.; Curtis, J. C. *J. Am. Chem. Soc.* **1997**, *119*, 5329.
(34) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.
(35) Dwyer, F. P.; Goodwin, H. A.; Gyarfas, E. C. *Aust. J. Chem.* **1963**, *16*, 42.
(36) Dwyer, F. P.; Goodwin, H. A.; Gyarfas, E. C. *Aust. J. Chem.* **1963**, *16*, 544.
(37) Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204.
(38) Beeston, R. F.; Aldridge, W. S.; Treadway, J. A.; Fitzgerald, M. C.; DeGraff, B. A.; Stitzel, S. E. *Inorg. Chem.* **1998**, *37*, 4368.
(39) Elliott, C. M.; Freitag, R. A.; Blaney, D. D. *J. Am. Chem. Soc.* **1985**, *107*, 4647.
(40) Larson, S. L.; Elliott, C. M.; Kelley, D. F. *J. Phys. Chem.* **1995**, *99*, 6530.
(41) Coe, B. J.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1995**, *34*, 593.
(42) Sullivan, B. P.; Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1404.
(43) Takeuchi, K. J.; Thompson, M. S.; Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 1845.
(44) Thompson, M. S. The Redox Properties and Redox Reactions of High Oxidation State Ruthenium Polypyridyl Complexes. Ph.D. Dissertation, University of North Carolina, Chapel Hill, NC, 1981.
(45) Smith, S. R.; Neyhart, G. A.; Kalsbeck, W. A.; Thorp, H. H. *New. J. Chem.* **1994**, *18*, 397.
(46) Coe, B. J.; Thompson, D. W.; Culbertson, C. T.; Schoonover, J. R.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 3385.
(47) Sauvage, J.; Collin, J.; Chambron, J.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993.
(48) Thummel, R. P.; Lefoulon, F.; Chirayil, S. *Inorg. Chem.* **1987**, *26*, 3072.

Scheme 2



We describe here an extension of the previously published heteroleptic synthetic methodology to the preparation of even more highly functionalized complexes. Advances made include the following. (1) The preparation of heteroleptic isothiocyanato complexes is described. Derivatives of these complexes have received attention due to their application as sensitizers of titanium dioxide semiconductors for the purpose of light-to-electrical energy conversion.[13,15,55] (2) A procedure for the isolation and purification of the solvento complexes *cis*-$[Ru^{II}(bpy')(bpy'')(CH_3CN)_2]^{2+}$ is provided as well as conditions for further reaction of this complex to form phosphine complexes. It overcomes limitations imposed by the reactivity of trimethylamine *N*-oxide and allows for the incorporation of halide ligands. (3) A generalized method for the synthesis of bis(pyridine) complexes such as *cis*-$[Ru^{II}(bpy')(bpy'')(py)_2]^{2+}$ by way of bound acetone intermediates is provided in which there is no restriction on the substitution patterns of the bipyridyl or pyridyl ligands. (4) The potential for increased functionalization of ruthenium(II) polypyridyl complexes has been markedly enhanced by preparation of the highly asymmetrical complexes *cis*-$[Ru(bpy')(bpy'')(X)(Y)]^{n+}$ in which X and Y are monodentate ligands. (5) Procedures for the preparation of nitrosyls of the form *cis*-$[Ru(bpy')(bpy'')(py)(NO)]^{3+}$ are described and strategies for the use of these complexes in the preparation of other asymmetrical complexes are discussed. It is shown that such precursors can be used to prepare unsymmetrical ligand-bridged complexes.

This chemistry is illustrated in Scheme 3. The compounds that result, including the series *cis*-$[Ru(bpy')(bpy'')(X)(Y)]^{n+}$ and dimeric ligand-bridged complexes, are the products of a versatile new synthetic approach which opens new possibilities for extending even further the diversity of Ru(II) polypyridine chemistry.

Experimental Section

Physical Methods. UV−visible spectra were recorded on Hewlett-Packard 8452A diode array or CARY 14 spectrophotometers (the latter interfaced to an IBM PC by OnLine Systems, Inc.). Infrared spectra were acquired by using a Mattson Galaxy 5000 series FT-IR spectrometer at 2 cm^{-1} resolution, averaging 25 scans (forward and reverse mirror velocity at 0.32 cm/s at 10 000 Hz). Solution cell spectra were acquired in a 1-mm path length cell equipped with BaF_2 or CaF_2 windows. ^1H NMR spectra were recorded on filtered solutions with a Bruker WM250 spectrometer.

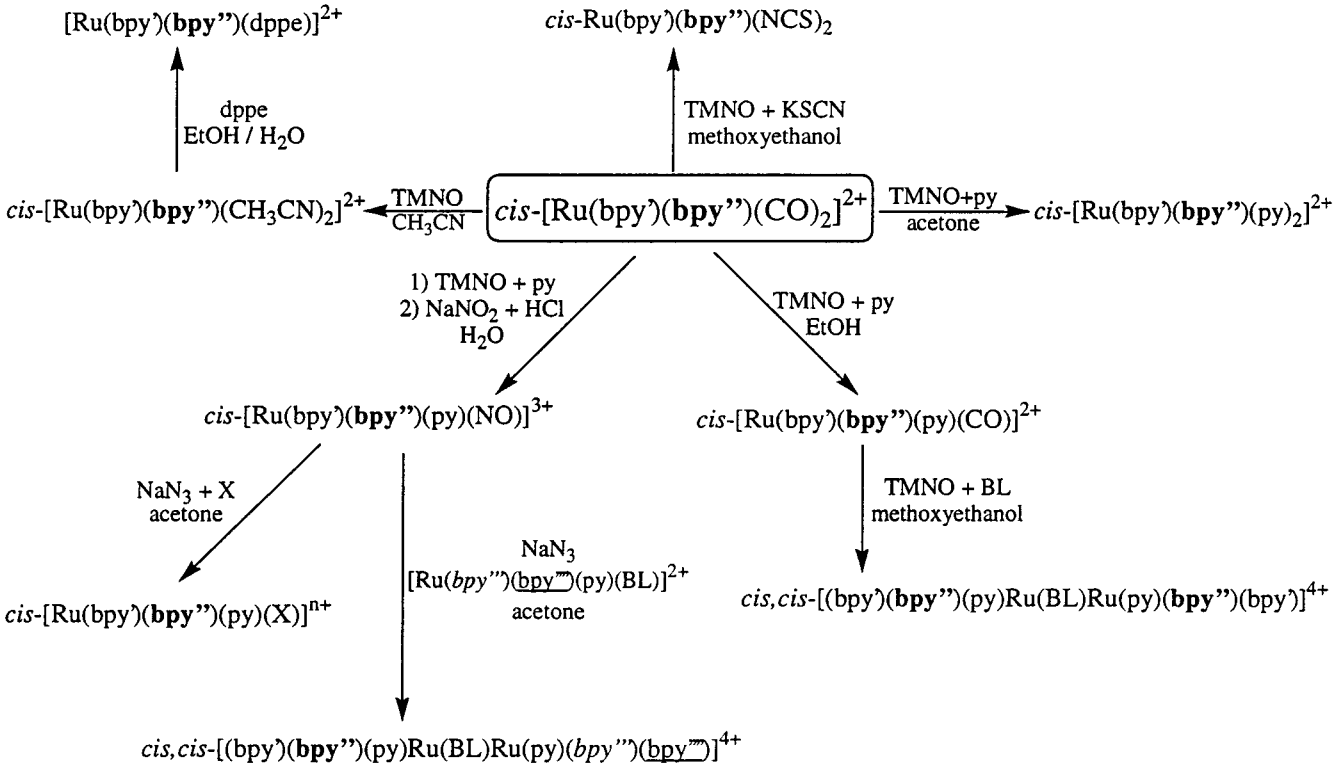
Electrochemical measurements were made in a drybox (N_2) with an EG&G PAR Model 273 potentiostat. Cyclic voltammetry was carried out in a standard three-compartment cell with a 4-mm platinum-disk working electrode, a platinum-wire counter electrode, and a $Ag/AgNO_3$ (0.01 M $AgNO_3$/0.1 M TBAH in acetonitrile) reference electrode, which was regularly calibrated with a saturated sodium chloride/calomel electrode (SSCE). When only small quantities of sample were available, a two-compartment microcell was utilized. A 3-mm platinum-disk working electrode and a silver wire pseudo-reference electrode were placed in one compartment and a platinum-wire counter electrode and $Ag/AgNO_3$ reference electrode in the other. The pseudo-reference electrode was calibrated with the reference electrode before every scan. Potentials are quoted relative to an SSCE.

Where noted, metal complexes were purified by cation-exchange HPLC on a Brownlee CX-300 Prep10 column (0.7 mL/min) by utilizing a linear gradient elution with 0−200 mM KBr in 1:3 (v/v) CH_3CN/aqueous phosphate buffer (0.6 mM; pH = 7.2). The elutions were controlled by a Rainin Dynamax SD-300 solvent delivery system equipped with 25 mL/min pump heads and monitored with a Shimadzu SPD-M10AV diode-array UV−visible spectrometer fitted with a 4.5-mm path length flow cell. The complexes were isolated from the eluent as hexafluorophosphate salts by addition of a saturated aqueous NH_4PF_6 solution followed by extraction into dichloromethane and evaporation under reduced pressure.

Materials. Hydrated $RuCl_3 \cdot 3H_2O$ (Strem), potassium thiocyanate (Fisher Certified), sodium nitrite (Aldrich 99.99+%), potassium nitrate (Aldrich 99+%), 4-*tert*-butylpyridine (Aldrich 99.9%), 4,4′-dimethyl-2,2′-bipyridine (GFS), paraformaldehyde (Aldrich 95%), formic acid (Fisher Certified 88%), 2-methoxyethanol (Aldrich anhydrous 99.8%), and 1,2-dimethoxyethane (Aldrich anhydrous 99.5%) were used as supplied. Trifluoromethane sulfonic acid (Aldrich 99+%) was either used as supplied or vacuum distilled if yellow-brown when received. Sodium *p*-toluenesulfonate (Aldrich 95%) and 2,2′-bipyridine (Aldrich 99+%) were recrystallized from water and ethyl acetate, respectively.

(49) Ross, H. B.; Boldaji, M.; Rillema, D. P.; Blanton, C. B.; White, R. P. *Inorg. Chem.* **1989**, *28*, 1013.
(50) Juris, A.; Campagna, S.; Balzani, V.; Gremaud, G.; von Zelewsky, A. *Inorg. Chem.* **1988**, *27*, 3652.
(51) von Zelewsky, A.; Gremaud, G. *Helv. Chim. Acta* **1988**, *71*, 1108.
(52) Strouse, G. F.; Anderson, P. A.; Schoonover, J. R.; Meyer, T. J.; Keene, F. R. *Inorg. Chem.* **1992**, *31*, 3004.
(53) Anderson, P. A.; Deacon, G. B.; Haarmann, K. H.; Keene, F. R.; Meyer, T. J.; Reitsma, D. A.; Skelton, B. W.; Strouse, G. F.; Thomas, N. C.; Treadway, J. A.; White, A. H. *Inorg. Chem.* **1995**, *34*, 6145.
(54) Strouse, G. F. Synthetic Design and Photophysical Properties of d^6 Transition Metal Chromophore-Quencher Complexes. Ph.D. Dissertation, University of North Carolina, Chapel Hill, NC, 1993.
(55) Moser, J. E. B. P.; Grätzel, M. *Coord. Chem. Rev.* **1998**, *171*, 245.

Scheme 3



Trimethylamine *N*-oxide (TMNO) was obtained by vacuum sublimation of the dihydrate (Aldrich 98%) at 90 °C. 4-Ethylpyridine (Aldrich 98%) was allowed to stir overnight with KOH, gravity filtered, and vacuum distilled from fresh KOH prior to use. Ethanol was freshly distilled over Mg/I_2. Spectral-grade acetonitrile (Burdick and Jackson), methanol (Burdick and Jackson), and ethanol (distilled over Mg/I_2) were used for all spectroscopic and electrochemical measurements. Silica gel (200−400 mesh, 60 Å) was obtained from Aldrich. Basic alumina was obtained from Fisher. SP Sephadex C25, CM Sephadex C25, and Sephadex LH-20 chromatographic materials were obtained from Pharmacia Biotech.

Syntheses. Chemical analyses were performed by Oneida Research Services, Inc. (Whitesboro, NY). The complexes *cis*-[Ru(bpy)(dmb)$(CO)_2](PF_6)_2$, *cis*-[Ru(dmb)(4,4′-$(COOEt)_2$bpy)$(CO)_2](PF_6)_2$, *cis*-[Ru(bpy)(tmb)$(CO)_2](PF_6)_2$ and *cis*,*cis*-Ru(bpy)$(CO)_2(CF_3SO_3)_2$ were prepared as described elsewhere.[52,53] *cis*-[Ru(bpy)$_2$$(CO)_2](PF_6)_2$ was prepared by an analogous route described below.

***cis*-Ru(dmb)(4,4′-$(COOEt)_2$bpy)$(NCS)_2\cdot H_2O$.** *cis*-[Ru(dmb)(4,4′-$(COOEt)_2$bpy)$(CO)_2](PF_6)_2$ (0.44 g, 0.47 mmol) and potassium thiocyanate (0.22 g, 2.3 mmol) were combined with dimethoxyethane (200 mL), and the mixture was deaerated by bubbling with Ar for 50 min. The reaction was heated to reflux, forming a bright orange solution. Solid TMNO (74 mg, 0.99 mmol) was added in one portion to the hot solution and heating was continued under Ar for an additional 7 h, after which the solution was deep purple. The solution was cooled to room temperature and evaporated to dryness under vacuum. Dichloromethane (5 mL) was added to the residue. The mixture was sonicated for 10 min and filtered. Addition of diethyl ether (150 mL) to the filtrate yielded the crude product as a purple solid. The crude material was purified by passage down a 15-cm neutral alumina column eluted with 4:1 (v/v) toluene/acetonitrile and then passage down a 15-cm silica gel column eluted with methanol. Yield: 0.16 g, 42%. ^{1}H NMR (dichloromethane-d_2): δ 1.37 (t, 3H), 1.51 (t, 3H), 2.42 (s, 3H), 2.68 (s, 3H), 4.42 (quart, 2H), 4.55 (quart, 2H), 6.86 (d, 1H), 7.18 (d, 1H), 7.58 (m, 2H), 7.78 (d, 1H), 7.93 (s, 1H), 8.07 (s, 1H), 8.21 (d, 1H), 8.71 (s, 1H), 8.86 (s, 1H), 9.29 (d, 1H), 9.72 (d, 1H). IR (KBr): $\bar{\nu}_{CN}$ = 2100 cm^{-1}, ν(CO) = 1723 cm^{-1}. Anal. Calcd for $C_{30}H_{30}N_6O_5RuS_2$: C, 50.06; H, 4.20; N, 11.68. Found: C, 50.09; H, 4.22; N, 11.39.

***cis*-[Ru(bpy)$_2$$(CO)_2](PF_6)_2$.** *cis*,*cis*-Ru(bpy)$(CO)_2(CF_3SO_3)_2$ (0.15, 0.25 mmol) and bipyridine (0.39, 0.25 mmol) were added to ethanol (25 mL) and the mixture was deaerated by bubbling with Ar for 50 min. All of the material dissolved when the reaction was heated to reflux, resulting in a pale orange solution. Heating at reflux was continued for 3 h. The solution was cooled to room temperature and the solvent removed under reduced pressure. The dark blue residue was triturated with 150 mL of boiling water. After the filtrate was cooled to room temperature, 2 mL of a saturated aqueous ammonium hexafluorophosphate solution was added, resulting in the immediate precipitation of a pale orange solid. The solid was collected by vacuum filtration, washed repeatedly with water and then diethyl ether, and dried under vacuum. Recrystallization of the crude product from hot ethanol/acetone yielded 0.15 g (80%) of the pure product as white needles. ^{1}H NMR (acetone-d_6): δ 7.68 (dd, 2H), 7.84 (d, 2H), 8.11 (dd, 2H), 8.38 (dd, 2H), 8.63 (dd, 2H), 8.82 (d, 2H), 8.94 (d, 2H), 9.51 (d, 2H). IR (KBr): ν(CO) = 2038 cm^{-1}, 2094 cm^{-1}.

***cis*-[Ru(bpy)$_2$$(CH_3CN)_2](PF_6)_2$.** *cis*-[Ru(bpy)$_2$$(CO)_2](PF_6)_2$ (0.20 g, 0.25 mmol) was dissolved in acetonitrile (100 mL) and the solution was deaerated by bubbling with Ar for 40 min. The reaction was heated to reflux. TMNO (0.55 g, 0.74 mmol) was added in one portion, and heating at reflux was continued for 1 h. The yellow solution was cooled to room temperature and concentrated to ~3 mL. Slow addition of diethyl ether precipitated the complex. To remove the remainder of the TMNO, the solid was dissolved in a minimum of ethanol and dripped into stirring ether (75 mL). HPLC analysis of the solid obtained showed it to be >99% pure. Analytically pure material was obtained by passage down a 10-cm silica gel column eluted with KNO_3-saturated methanol. After the methanol was evaporated, the residue was triturated with dichloromethane, which was subsequently evaporated under vacuum. ^{1}H NMR, UV−visible absorption, and electrochemical data for this material matched that of material prepared previously by literature methods.[34] Yield 0.19 g, 94%.

***cis*-[Ru(bpy)(tmb)$(CH_3CN)_2](PF_6)_2$.** This reaction was carried out in a manner analogous to the preceding procedure. The reaction of *cis*-[Ru(bpy)(tmb)$(CO)_2](PF_6)_2$ on a 0.10-g scale yielded the product in 96% yield. ^{1}H NMR (dichloromethane-d_2): δ 2.02 (s, 3H), 2.37 (s, 3H), 2.45 (s, 3H), 2.48 (s, 3H), 2.56 (s, 3H), 2.62 (s, 3H), 7.16 (s, 1H), 7.27 (dd, 1H), 7.55 (d, 1H), 7.93 (m, 2H), 8.06 (s, 1H), 8.20 (s, 1H), 8.23 (dd, 1H), 8.42 (d, 1H), 8.54 (d, 1H), 8.94 (s, 1H), 9.44 (d, 1H). Anal. Calcd for $C_{28}H_{30}F_{12}N_6P_2Ru$: C, 39.96; H, 3.59; N, 9.99. Found: C, 39.26; H, 3.65; N, 9.63.

[Ru(bpy)$_2$(dppe)](PF$_6$)$_2$. *cis*-[Ru(bpy)$_2$(CH$_3$CN)$_2$](PF$_6$)$_2$ (58 mg, 0.074 mmol) and bis(diphenylphosphino)ethylene (35 mg, 0.089 mmol) were dissolved in ethanol (35 mL) and water (5 mL). The solution was heated at reflux for 12 h, after which time it had turned pale yellow. The reaction was cooled to room temperature and the solvent was removed under reduced pressure. The resulting residue was dissolved in a minimum of acetone and reprecipitated by slow addition to rapidly stirring ether. The pale orange solid was collected by vacuum filtration and washed repeatedly with ether. One recrystallization from ethanol removed an orange impurity. When necessary, a second recrystallization from dichloromethane/ether was performed. Yield: 81 mg, 88%. ^{1}H NMR (dichloromethane-d_2): δ 6.48 (d, 2H), 6.52 (d, 2H), 6.81 (dd, 2H), 6.91 (dd, 4H), 7.09 (dd, 2H), 7.46 (m, 12H), 7.80 (m, 6H), 8.02 (d, 2H), 8.11 (dd, 2H), 8.28 (d, 2H). The 0−10 ppm region of the spectrum lacks two of the expected proton resonances arising from dppe, but these two resonances are also absent in the same chemical shift range in a spectrum of the dppe ligand. The electrochemical ($E_{1/2}$ = +1.69, −1.26, −1.51 V) and UV−visible absorbance (λ_{max} = 378, 318, 294, 278 nm) results were in good agreement ($E_{1/2}$ = +1.75, −1.28, −1.51 V; λ_{max} = 373, 317, 293, 276 nm) with those acquired for a sample prepared by an independent route.[34]

***cis*-[Ru(bpy)(dmb)(4-Etpy)$_2$](PF$_6$)$_2$.** The entire reaction was carried out under an Ar atmosphere. *cis*-[Ru(bpy)(dmb)(CO)$_2$](PF$_6$)$_2$ (0.12 g, 0.152 mmol) and 4-ethylpyridine (0.17 mL, 1.52 mmol) were combined in 100 mL of acetone which had been dried over molecular sieves. The solution was cooled to −9 °C in an ice/brine bath and deaerated by bubbling with Ar for 45 min. An acetone solution of trimethylamine *N*-oxide (0.024 g, 0.32 mmol) was similarly deaerated and dripped into the solution containing the metal complex over the course of 3 h. The solution was allowed to warm to room temperature then heated at reflux for 12 h. The volume of the red solution was reduced to ∼5 mL. Upon slow addition of this solution to 250 mL of vigorously stirring diethyl ether, an orange precipitate formed which was collected and washed repeatedly with ether to remove the last of the excess 4-ethylpyridine. One recrystallization from hot ethanol/acetone yielded the product in ∼95% yield and of ∼95% purity. Analytically pure material could be obtained by elution from a 15-cm neutral alumina column (2:1 toluene/acetonitrile eluent) and then by elution from a 15-cm silica column (KNO$_3$-saturated methanol eluent). The methanol was removed by rotary evaporation and the residue triturated with dichloromethane. The dichloromethane solution was concentrated under vacuum and dripped into rapidly stirring ether to precipitate the pure complex as the hexafluorophosphate salt. Yield: 79 mg, 55%. ^{1}H NMR (dichloromethane-d_2): δ 1.19 (t, 3H), 1.20 (t, 3H), 2.48 (s, 3H), 2.64 (quart, 2H), 2.65 (s, 3H), 2.66 (quart, 2H), 7.18 (m, 4H), 7.43 (m, 1H), 7.65 (m, 2H), 7.87 (m, 2H), 8.1 (m, 9H), 8.69 (d, 1H), 8.91 (d, 1H). Anal. Calcd for $C_{36}H_{38}F_{12}N_6P_2Ru$: C, 45.72; H, 4.05; N, 8.89. Found: C, 45.61; H, 4.06; N, 8.75.

***cis*-[Ru(bpy)(tmb)(CO)(4-^{t}Bupy)](PF$_6$)$_2$.** *cis*-[Ru(bpy)(tmb)(CO)$_2$](PF$_6$)$_2$ (0.280 g, 0.343 mmol) and 4-^{t}Bupy (96 μL, 0.65 mmol) were combined with 200 mL of ethanol and the mixture deaerated for 40 min by bubbling with Ar. An inert atmosphere was maintained over the reaction throughout the preparation. The mixture was heated at reflux until complete dissolution of the solid reactant was effected. An ethanolic solution of trimethylamine *N*-oxide (48.3 mL × 7.10 mM, 0.343 mmol) was deaerated with Ar for 40 min and slowly dripped into the reaction over the course of 90 min using an addition funnel with a pressure equalization arm. The pale yellow solution became bright red and was allowed to reflux an additional 90 min. About 1 mL of the reaction was withdrawn and evaporated to dryness under reduced pressure. The residue was taken up in dichloromethane and an IR spectrum of the solution recorded. The spectrum revealed $\bar{\nu}_{CO}$ at 2096 and 2041 cm^{-1} (starting material) which integrated to 7% of the area of the main band at 1995 cm^{-1} (product). An additional portion of the TMNO solution (5 mL) was added to force the reaction to completion and the solution was allowed to stir at reflux overnight. This solution was taken to dryness by rotary evaporation under reduced pressure and the residue redissolved in a minimum (∼3 mL) of dichloromethane. The concentrated solution was slowly dripped into 200 mL of rapidly stirring diethyl ether to precipitate a yellow solid. Recrystallization of the solid from ethanol provided the desired product in ∼98% purity (yield 205 mg, 65%) as a 1:1 mixture of the two possible geometrical isomers. The material was obtained analytically pure, but in reduced yield, by elution from a silica-gel column with KNO$_3$-saturated methanol. The second band was collected and evaporated to dryness. The resulting solid was triturated with dichloromethane and the resulting orange solution dripped into rapidly stirring diethyl ether to precipitate the product in an overall 44% yield, 140 mg. ^{1}H NMR (dichloromethane-d_2): δ 1.26 (s, 9H), 1.27 (s, 9H), 2.07 (s, 3H), 2.16 (s, 3H), 2.38 (s, 3H), 2.40 (s, 3H), 2.44 (s, 3H), 2.52 (s, 3H), 2.58 (s, 3H), 2.62 (s, 3H), 7.14 (s, 1H), 7.22 (s, 1H), 7.43 (m, 5H), 7.58 (d, 1H), 7.73 (m, *), 7.87 (m, *), 8.23 (m, *), 8.55 (d, 1H), 8.96 (s, 1H), 9.47 (d, 1H), * = total of 21H. IR (KBr): ν(CO) = 1988 cm^{-1}. Anal. Calcd for $C_{34}H_{37}F_{12}N_5OP_2Ru$: C, 44.26; H, 4.04; N, 7.59. Found: C, 43.68; H, 4.15; N, 7.40.

***cis*-[Ru(bpy)(dmb)(CO)(4-^{t}Bupy)](PF$_6$)$_2$.** This salt was prepared similarly by utilizing *cis*-[Ru(bpy)(dmb)(CO)$_2$](PF$_6$)$_2$ (55 mg, 0.070 mmol) and 4-^{t}Bupy (16 μL, 0.11 mmol) in 75 mL of ethanol. A slight excess (0.077 mmol) of TMNO was used to decarbonylate the precursor complex. A yield of 32 mg (52%) was obtained. ^{1}H NMR (dichloromethane-d_2): δ 1.26 (s, 9H), 1.27 (s, 9H), 2.51 (s, 3H), 2.56 (s, 3H), 2.68 (s, 3H), 2.75 (s, 3H), 7.21 (d, 1H), 7.42 (m, 7H), 7.70 (m, 8H), 8.10 (m, 2H), 8.25 (m, 15H), 8.55 (d, 1H), 9.22 (d, 1H), 9.45 (d, 1H). IR (KBr): $\bar{\nu}_{CO}$ = 1989 cm^{-1}.

***cis*-[Ru(bpy)(tmb)(4-^{t}Bupy)(NO)](PF$_6$)$_3$.** *cis*-[Ru(bpy)(tmb)(CO)$_2$](PF$_6$)$_2$ (0.152 g, 0.186 mmol) and 4-^{t}Bupy (102 μL) were added to 40 mL of methoxyethanol. After the solution was deaerated with Ar, it was heated to reflux and TMNO (42 mg, 0.56 mmol) was added. The yellow solution was heated at reflux for 4 h, resulting in a color change to dark orange. The solution was cooled to room temperature and the solvent removed under reduced pressure. The resulting residue was taken up in a minimum of acetone and dripped into 150 mL of rapidly stirring ether to produce an orange solid. The solid was collected by vacuum filtration and washed with ether. One repetition of the reprecipitation and washing was performed to ensure complete removal of unreacted 4-^{t}Bupy. The resulting solid was air-dried and then suspended in 200 mL of water and heated at reflux for 4 h. A 2 M HCl solution (6 mL) was added followed by sodium nitrite (12.8 mg, 0.186 mmol) in 3 mL of water, resulting in an immediate color change to pale yellow. After cooling the solution to room temperature, 2 mL of a saturated aqueous ammonium hexafluorophosphate solution was added to precipitate the product as a bright yellow solid. The product was collected by vacuum filtration, dissolved in a minimum of acetone, filtered, and reprecipitated into ether. The yield following two recrystallizations from acetone/ether was 0.10 g (50%). IR (KBr): ν(NO) = 1939 cm^{-1}. To confirm the identity of this material, an absorbance spectrum was taken before (λ_{max} = 386 nm) and after (λ_{max} = 502 nm) conversion of the complex to [Ru(bpy)(tmb)(4-^{t}Bupy)(N$_3$)]$^+$ by using methanolic sodium azide and acetone. The reaction occurred in <1 min, and the resulting UV−visible and IR spectra (ν(N$_3$) = 2036 cm^{-1}) compared well with literature[56] values (λ_{max} = 498 nm, ν(N$_3$) = 2031 cm^{-1}) for [Ru(bpy)$_2$(py)(N$_3$)]$^+$.

***cis,cis*-[(Ru(bpy)(tmb)(4-^{t}Bupy))$_2$(pz)](PF$_6$)$_4$. Method 1.** *cis*-[Ru(bpy)(tmb)(4-^{t}Bupy)(NO)](PF$_6$)$_3$ (0.048 g, 0.045 mmol) was dissolved in 3 mL of acetone and the pale orange solution was deaerated with bubbling acetone-saturated Ar for 50 min. A separate solution of 46.0 mM sodium azide in methanol was similarly deaerated and 976 μL was slowly dripped into the stirring acetone solution. A solution of pyrazine in acetone (88.7 mM) was deaerated and 253 μL was added to the reaction in one portion. The red solution was heated at reflux overnight under an Ar atmosphere. Removal of the solvent under vacuum yielded a bright red solid which was applied to a 9 × 2 cm Sephadex LH-20 column and eluted with methanol. The first band was collected, and the orange and pink trailing bands were discarded. Ether was added to the methanol solution until precipitation began to occur. One more drop of methanol was added to redissolve the precipitate and the solution was placed in the freezer overnight. This crystallization procedure yielded the pure product (18 mg, 44%) as red needles. The spectroscopic and electrochemical behavior of this material was identical

(56) Brown, G. M.; Callahan, R. W.; Meyer, T. J. *Inorg. Chem.* **1975**, *14*, 1915.

to that obtained for the product of method 2 below. As this complex was found to be extremely photoreactive, care was taken during the preparation and purification to exclude all light.

Method 2. Care was taken at all times to exclude light from all the complexes utilized in this preparation. *cis*-$[Ru(bpy)(tmb)(CO)_2](PF_6)_2$ (0.15 g, 0.18 mmol) was combined with 4-^{t}Bupy (136 μL, 0.920 mmol) and 50 mL of ethanol and the mixture was deaerated by bubbling with Ar for 50 min. Trimethylamine *N*-oxide (15 mg, 0.20 mmol) was dissolved in ethanol and similarly deaerated. The solution containing the metal complex was heated to reflux and heating continued while the trimethylamine *N*-oxide solution was slowly dripped over the course of 2 h into the reaction via an addition funnel equipped with a pressure equalization arm. The reaction was heated at reflux for an additional 4 h, at which time an infrared spectrum of an aliquot showed no remaining dicarbonyl complex. After cooling of the reaction to room temperature, the solution was concentrated under reduced pressure to ~4 mL and the intermediate precipitated by addition to 100 mL of rapidly stirring diethyl ether. The solid was collected by vacuum filtration and triturated with 3 × 15 mL of ether to remove unreacted 4-^{t}Bupy. The solid was dissolved in 35 mL of methoxyethanol along with pyrazine (14.5 mg, 0.18 mmol) and the solution deaerated with Ar for 50 min before being heated to reflux. Trimethylamine *N*-oxide (21 mg, 0.28 mmol) was added as a solid in one portion and the reaction was allowed to reflux overnight, then cooled to room temperature, and taken to dryness under reduced pressure. The resulting red residue was dissolved in 5 mL of acetonitrile and the crude product precipitated by addition of 150 mL of ether. The solid was collected by vacuum filtration, washed repeatedly with ether, and then allowed to air-dry.

Purification of the dimer was carried out in three steps. First, the crude product was dissolved in a minimum of methanol and eluted with methanol from a 45 × 2.5 cm column packed with Sephadex LH-20 size-exclusion resin. The bright-red first band was collected, concentrated, and reapplied to the column, which had been washed with 0.1% acetic acid in methanol. Only the central portion of the band was collected the second time. The solvent was removed under reduced pressure and the residue taken up in a minimum of acetonitrile. A large volume of 10% acetonitrile in water was rapidly added to the solution and the resulting dilute solution was gravity filtered and eluted from a CM Sephadex C25 cation-exchange column utilizing a gradient of 0−0.3 M KNO_3 in 10% aqueous acetonitrile. The material was crystallized by doubling the volume of the eluent fraction containing the major band collected with acetonitrile, adding ammonium hexafluorophosphate, and slowly removing the acetonitrile under reduced pressure. Yield: 62 mg, 40%. The ^{1}H NMR spectra of these materials were extremely complex owing to the large number of geometrical isomers. Analytical HPLC analysis, however, showed the material to be >99% pure when prepared by either method. The characteristic electrochemical response (~100 mV peak splitting for the two $Ru^{III/II}$ couples and 2:1 peak current ratio for the bipyridyl and pyrazyl reductions) was also identical for the two samples.

Results

Syntheses. Ligand structures are shown in Figure 1. The syntheses of the precursor complexes were straightforward and based upon the recently published procedure for tris-heteroleptic complexes.[52,53] Earlier accounts of the reactivity of Ru^{II} and Ru^{III} nitro-,[57] nitrito-,[58] and nitrosyl,[57,59] complexes and the azide-assisted removal of nitrosyl from Ru^{II} complexes[58,60−62] were used to extend the synthetic methodology by using the nitrosyl ligand. The target complexes were prepared by trimethylamine *N*-oxide-assisted oxidative decarbonylation of *cis*-$[Ru(bpy')(bpy'')(CO)_2]^{2+}$ precursors. Yields varied from 44% to 96% in these preparations.

The preparations fall into two categories. In one, both carbonyl ligands in *cis*-$[Ru(bpy')(bpy'')(CO)_2]^{2+}$ are replaced with the same monodentate ligand. In the other, the replacement is asymmetrical. In general, the symmetrical cases were prepared by addition of 2 equiv or more of trimethylamine *N*-oxide in 2-methoxyethanol (or dimethoxyethane in some cases to avoid transesterification of 4,4′-$(COOEt)_2$bpy) heated at reflux. To prevent the replacement of the second carbonyl ligand in the asymmetrical syntheses, 1 equiv of trimethylamine *N*-oxide was added in lower boiling ethanol. The exception was *cis*-$[Ru(bpy)(dmb)(4\text{-}Etpy)_2](PF_6)_2$, for which a higher yield (55%) was obtained by extended reflux in acetone following low-temperature addition of trimethylamine *N*-oxide. This yield is significantly higher than reported previously for related compounds by an alternate procedure.[63]

The earlier procedure[52,53] could not be used to incorporate dppe into complexes in reasonable yields due to the oxidation of dppe by trimethylamine *N*-oxide. For this preparation, the solvento complex *cis*-$[Ru(bpy)(tmb)(CH_3CN)_2](PF_6)_2$ was isolated in high yield and used as a synthetic intermediate. The ^{1}H NMR spectrum of the phosphine complex is complex, as expected given its low symmetry and the large number of nonequivalent aromatic resonances. The same procedure was therefore applied to the preparation of $[Ru(bpy)_2(dppe)](PF_6)_2$ as well. The preparation of the precursor *cis*-$[Ru(bpy)_2(CO)_2](PF_6)_2$ has been included since it was not presented in the original publication.

It was also found that trimethylamine *N*-oxide reacts with nitrite anion, preventing the direct preparation of the mixed-chelate complexes *cis*-$Ru(bpy)(tmb)(NO_2)_2$ and *cis*-$[Ru(bpy)(tmb)(4\text{-}^t Bupy)(NO_2)]^+$ or the nitrosyl-containing analogues. The related complex *cis*-$[Ru(bpy)(tmb)(4\text{-}^t Bupy)(NO)](PF_6)_3$ was prepared, however, by isolating (without purification) *cis*-$[Ru(bpy)(tmb)(4\text{-}Etpy)_2](PF_6)_2$ and allowing it to react first with water then with sodium nitrite in the presence of HCl.

This complex and the pyridine/carbonyl complexes *cis*-$[Ru(bpy)(tmb)(CO)(4\text{-}^t Bupy)](PF_6)_2$ and *cis*-$[Ru(bpy)(dmb)(CO)(4\text{-}^t Bupy)](PF_6)_2$ were prepared as mixtures of the two possible geometrical isomers in every case. ^{1}H NMR spectra indicated that the isomer product ratios were 1:1 in all cases, both in the crude products and following purification. These mixtures could presumably be separated by previously developed chromatographic procedures,[63−65] but no attempt was made to separate the isomers.

In accordance with previous reports,[66] all of the linkage isomers of *cis*-$Ru(dmb)(4,4'\text{-}(COOEt)_2bpy)(NCS)_2$ were also prepared by decarbonylating *cis*-$[Ru(dmb)(4,4'\text{-}(COOEt)_2bpy)(CO)_2](PF_6)_2$ in the presence of excess thiocyanate anion. In this case, however, one isomer predominates, the one in which both anions are bound to Ru^{II} as nitrogen donors. In contrast to previous results with homoleptic complexes,[15,66] the major isomer was separable from the others and was isolated cleanly.

The identity of the nitrosyl intermediate *cis*-$[Ru(bpy)(tmb)(4\text{-}^t Bupy)(NO)]^{3+}$ was confirmed by infrared spectroscopy and electrochemical experiments. The presence of both NO (at 1938 cm^{-1}) and PF_6^- (846 cm^{-1}) was apparent in the IR and the NO-based reduction was observed at +0.48 V in acetonitrile versus SSCE along with several irreversible bands characteristic

(57) Godwin, J. B.; Meyer, T. J. *Inorg. Chem.* **1971**, *10*, 471.
(58) Adeyemi, S. A.; Miller, F. J.; Meyer, T. J. *Inorg. Chem.* **1972**, *11*, 994.
(59) Keene, F. R.; Salmon, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 4821.
(60) Powers, M. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 1785.
(61) Adeyemi, S. A.; Johnson, E. C.; Miller, F. J.; Meyer, T. J. *Inorg. Chem.* **1973**, *12*, 2371.
(62) Miller, F. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1971**, *93*, 1294.
(63) Rutherford, T. J.; Keene, F. R. *Inorg. Chem.* **1997**, *36*, 2872.
(64) Rutherford, T. J.; Keene, F. R. *Inorg. Chem.* **1997**, *36*, 3580.
(65) Reitsma, D. A.; Keene, F. R. *J. Chem. Soc., Dalton Trans.* **1993**, 2859.
(66) Kohle, O.; Ruile, S.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 4779.

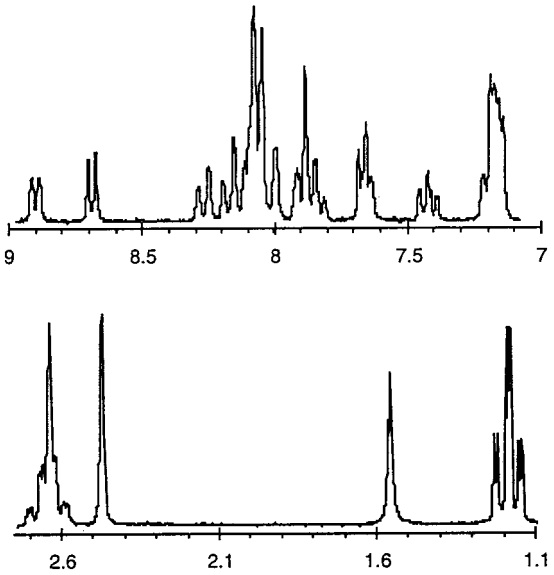


Figure 2. ^{1}H NMR spectrum of *cis*-[Ru(bpy)(dmb)(4-Etpy)$_2$](PF$_6$)$_2$ in dichlormethane-d_2. The relative x (δ, ppm) and y axes have been independently normalized for the two spectral regions. The singlet at 1.55 ppm is water from the solvent.

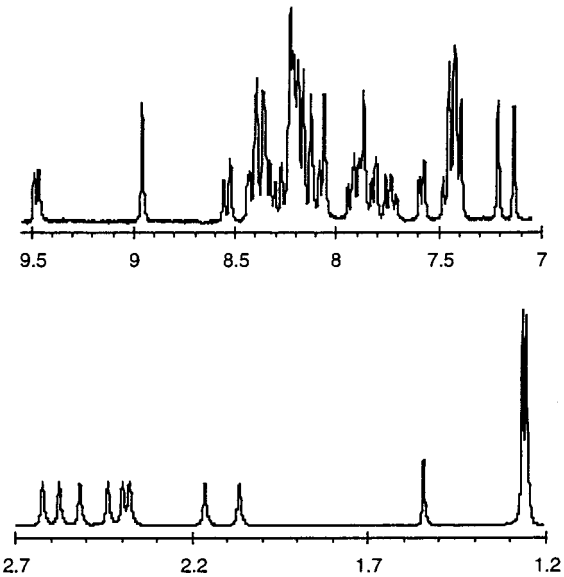


Figure 3. As in Figure 2. ^{1}H NMR spectrum of a 1:1 mixture of the two geometrical isomers of *cis*-[Ru(bpy)(tmb)(4-^{t}Bupy)(CO)](PF$_6$)$_2$ in dichlormethane-d_2.

of these complexes (Supporting Information Figure S11). Also, the azide derivative was prepared by addition of NaN_3 and characterized by IR and UV−visible spectroscopy. The reaction with N_3^- occurred in <1 min, producing dramatic changes in both spectra. No reaction with N_3^- was observed with either the *cis*-[Ru(bpy)(tmb)(CO)$_2$]$^{2+}$ starting material or with the oversubstitution product *cis*-[Ru(bpy)(tmb)(4-^{t}Bupy)$_2$]$^{2+}$.

Characterization. The proton NMR spectra of several of the new complexes are shown in Figures 2−5. The spectrum of [Ru(bpy)(tmb)(dppe)](PF$_6$)$_2$ is included as Supplementary Figure S1. All spectra were acquired in dichloromethane-d_2. Due to the large number of resonances in the 7−10 and 1−4 ppm regions, the middle region of each spectrum (~4 to ~7 ppm, which includes only the solvent triplet at δ = 5.32 ppm) is excluded and the two remaining halves scaled separately. Integrations are listed in the Experimental Section. The spectrum of *cis*-[Ru(bpy)(tmb)(CO)(4-^{t}Bupy)](PF$_6$)$_2$ (Figure 3) is a composite of the spectra for the two possible geometrical isomers, as mentioned above.

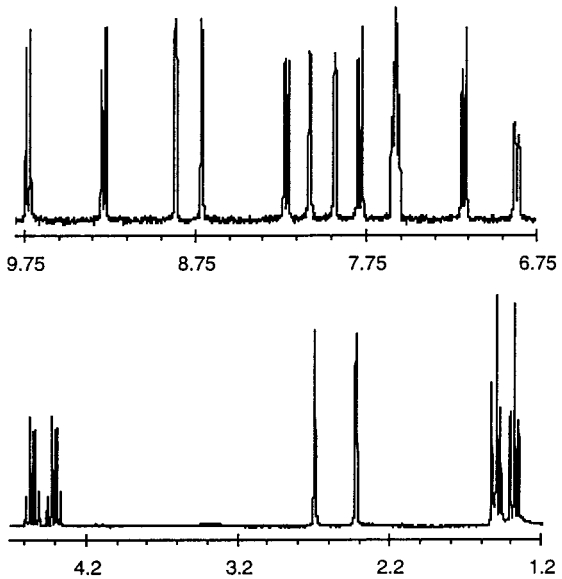


Figure 4. As in Figure 2. ^{1}H NMR spectrum of *cis*-Ru(dmb)(4,4′-(CO$_2$Et)$_2$bpy)(NCS)$_2$ in dichloromethane-d_2.

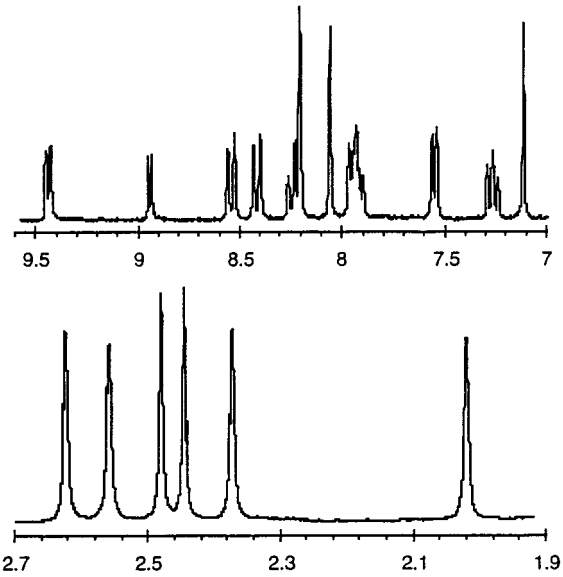


Figure 5. As in Figure 2. ^{1}H NMR spectrum of *cis*-[Ru(bpy)(tmb)-(CH$_3$CN)$_2$](PF$_6$)$_2$ in dichloromethane-d_2.

Table 1. Infrared Band Energies (KBr) and Assignments for Selected Complexes

complex or salt	energy (cm^{-1})	origin
cis-Ru(dmb)(4,4′-(COOEt)$_2$bpy)(NCS)$_2$	2100 vs	ν(CN)
	1723 s	ν(C═O), ester
cis-[Ru(bpy)$_2$(CO)$_2$](PF$_6$)$_2$	2094 vs	ν(CO)
	2038 vs	ν(CO)
cis-[Ru(bpy)(tmb)(CO)$_2$](PF$_6$)$_2$	2098 vs	ν(CO)
	2036 vs	ν(CO)
cis-[Ru(bpy)(tmb)(CH$_3$CN)$_2$](PF$_6$)$_2$	2280 w	ν(CN)
cis-[Ru(bpy)(tmb)(CO)(4-^{t}Bupy)](PF$_6$)$_2$	1988 vs	ν(CO)
cis-[Ru(bpy)(tmb)(4-^{t}Bupy)(NO)](PF$_6$)$_3$	1938 s	ν(NO)

Important infrared band energies for several complexes in KBr are listed in Table 1 with band assignments where appropriate. For *cis*-[Ru(bpy)(dmb)(CO)(4-Etpy)]$^{2+}$, two geometrical isomers are present as determined by ^{1}H NMR, but no splitting is evident in ν(CO) at 2 cm^{-1} resolution (Figure 6B).

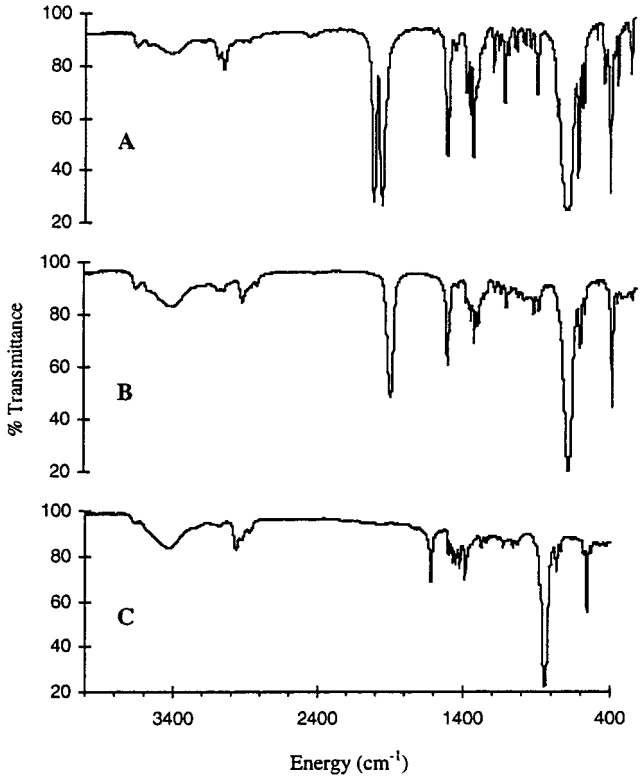


Figure 6. Infrared spectra of [Ru(bpy)(dmb)(CO)$_2$](PF$_6$)$_2$ (A), [Ru(bpy)(dmb)(CO)(4-Etpy)](PF$_6$)$_2$ (B), and [Ru(bpy)(dmb)(4-Etpy)$_2$](PF$_6$)$_2$ (C) in KBr pellets.

Table 2. UV−Visible Band Maxima in CH_3CN at Room Temperature

complex or salt	λ_{max} (nm)					
cis-Ru(dmb)(4,4′-(COOEt)$_2$bpy)(NCS)$_2$	550	434	316	294	242	206
cis-[Ru(bpy)(tmb)(CH$_3$CN)$_2$](PF$_6$)$_2$	422	398	286	254	244	208
[Ru(bpy)$_2$(dppe)](PF$_6$)$_2$	378	318	294	278		
cis-[Ru(bpy)(dmb)(4-Etpy)$_2$](PF$_6$)$_2$	466	429	338	291	245	
cis-[Ru(bpy)(tmb)(CO)(4-^{t}Bupy)](PF$_6$)$_2$	368	316	310	266		
cis-[Ru(bpy)(tmb)(4-^{t}Bupy)(NO)](PF$_6$)$_3$	386	314	292	268	210	
cis,*cis*-[(Ru(bpy)(tmb)(4-^{t}Bupy))$_2$(pz)](PF$_6$)$_4$	498	436	338	290	208	
cis,*cis*-[(Ru(bpy)(tmb)(4-^{t}Bupy))$_2$(pz)](PF$_6$)$_5$	496	436	290	210		

Similar results were obtained for *cis*-[Ru(bpy)(tmb)(CO)(4-^{t}Bupy)]$^{2+}$. Two isomers were also present in *cis*-[Ru(bpy)(tmb)(4-^{t}Bupy)(NO)]$^{3+}$, but only a single intense ν(NO) band was observed.

The decarbonylation reactions were most conveniently monitored by withdrawing aliquots, stripping off the solvent under vacuum, redissolving the resulting residues in dichloromethane, and obtaining solution IR spectra. For example, the loss of bands at 2098 and 2036 cm^{-1} in *cis*-[Ru(bpy)(tmb)(CO)$_2$](PF$_6$)$_2$ was observed to occur concomitantly with the appearance of a single band at 1988 cm^{-1} for *cis*-[Ru(bpy)(tmb)(CO)(4-^{t}Bupy)](PF$_6$)$_2$. Figure 6 shows a stacked view of IR spectra for the sequential steps in the reaction of *cis*-[Ru(bpy)(dmb)(CO)$_2$](PF$_6$)$_2$ to form *cis*-[Ru(bpy)(dmb)(4-Etpy)$_2$](PF$_6$)$_2$. The disappearance of the CO stretch at 1989 cm^{-1} is evident in the final spectrum. The identity of the final product is confirmed by the ^{1}H NMR spectrum in Figure 2.

UV−visible data for the new complexes in acetonitrile at room temperature are listed in Table 2. The lowest energy bands are d$\pi \rightarrow \pi_1$* (to the bipyridyl ligand) in all cases, with molar extinction coefficients in the range of 8000 to 20 000 M^{-1} cm^{-1}. For *cis*-[Ru(bpy)(dmb)(4-Etpy)$_2$](PF$_6$)$_2$, the second lowest energy band (similar intensity) is a d$\pi \rightarrow \pi_1$* transition into the pyridine ligand. In *cis*-Ru(dmb)(4,4′-(COOEt)$_2$bpy)(NCS)$_2$, the second lowest band is a d$\pi \rightarrow \pi_2$* transition to the LUMO + 1 antibonding orbitals of the bipyridyl ligands. In all other cases the second lowest energy band (40 000 $< \epsilon <$ 150 000 in units of M^{-1} cm^{-1}) arises from a $\pi \rightarrow \pi_1$* transition localized on the bipyridyl ligands. These assignments are discussed elsewhere.[14,67]

Table 3. $E_{1/2}$ Values in CH_3CN 0.1 M in Tetrabutylammonium Hexafluorophosphate versus SSCE at Room Temperature

complex or salt	$E_{1/2}^{III/II}$	$E_{1/2}^{0/-}$	$E_{1/2}^{-/2-}$
Ru(dmb)(4,4′-(COOEt)$_2$bpy)(NCS)$_2$	+0.73	−1.19	−1.67[a]
[Ru(bpy)(tmb)(CH$_3$CN)$_2$](PF$_6$)$_2$	+1.38	−1.39	−1.74
[Ru(bpy)$_2$(dppe)](PF$_6$)$_2$	+1.69	−1.26	−1.51
[Ru(bpy)(dmb)(4-Etpy)$_2$](PF$_6$)$_2$	+1.15	−1.43	−1.68
[Ru(bpy)(tmb)(CO)(4-^{t}Bupy)](PF$_6$)$_2$		−1.17	−1.48
[Ru(bpy)(dmb)(CO)(4-^{t}Bupy)](PF$_6$)$_2$		−1.11	−1.45
[Ru(bpy)(tmb)(4-^{t}Bupy)(NO)](PF$_6$)$_3$	+0.48[b]	−0.42[a,b]	
[(Ru(bpy)(tmb)(4-^{t}Bupy))$_2$(pz)](PF$_6$)$_4$	+1.25/+1.37	−1.03	−1.44[c]

[a] $E_{p,c}$ value at 200 mV/s scan rate; the reduction is irreversible. [b] Reduction at the nitrosyl ligand. [c] Two-electron wave.

The results of cyclic voltammetric measurements (Supporting Information Figures S7−S11) are summarized in Table 3. All oxidations and reductions were reversible or quasi-reversible with 60 mV $< \Delta E_{1/2} <$ 90 mV, except where noted elsewhere. As expected,[56,68,69] the electrochemistry of the nitrosyl complexes is complicated. In reductive scans a NO-based reduction was observed at +0.48 V followed by a chemically irreversible reduction at $E_{p,c} = -0.42$ V. Scanning through this wave results in oxidative waves at $E_{p,a} = -0.32$, −0.18, and +0.68 V. Reductive scanning also results in a precipitation spike at +0.12 V and its reverse at +0.34 V. No metal-based oxidations were observable for any of the nitrosyl complexes nor for any of the carbonyl complexes.

One reversible metal-based couple and one reversible ligand-based couple were observed for *cis*-Ru(dmb)(4,4′-(COOEt)$_2$bpy)(NCS)$_2$.When the electrode was scanned more anodically than +1.20 V, an irreversible wave appeared at $E_{p,a} = +1.32$ V followed by the appearance of a reduction wave at $E_{p,c} = +0.88$ V. The second ligand-based reduction for this complex is near the solvent limit and irreversible.

In the electrochemistry of *cis*,*cis*-[((bpy)(tmb)(4-^{t}Bupy)Ru)$_2$(pz)](PF$_6$)$_4$, the first reduction, −1.03 V, occurs at pyrazine. The second reductive wave at −1.44 V is a two-electron wave arising from the simultaneous reduction of two bipyridine ligands, one at each metal. The oxidative wave is split into two one-electron waves at +1.25 and +1.37 V, consistent with interactions between metals across the bridge.[70−73]

(67) Treadway, J. A.; Strouse, G. F.; Anderson, P. A.; Keene, F. R.; Meyer, T. J. Manuscript in preparation.
(68) Murphy, W. R. J.; Takeuchi, K.; Barley, M. H.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 1042.
(69) Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2466.
(70) Salaymeh, F.; Berhane, S.; Yusof, R.; Rosa, R. D. L.; Fung, E. Y.; Matamoros, R.; Lau, K. W., Zheng, Q.; Kober, E. M.; Curtis, J. C. *Inorg. Chem.* **1993**, *32*, 3895.
(71) Callahan, R. W.; Brown, G. M.; Meyer, T. J. *Inorg. Chem.* **1975**, *14*, 1443.
(72) Meyer, T. J. Electron Transfer in Mixed-Valence Compounds. In *Mixed-Valence Compounds*; Brown, D. B., Ed.; Reidel Publishing Co.: Boston, 1980; p 75.
(73) Meyer, T. J. Redox Properties of Polymetallic Systems. In *Inorganic Compounds with Unusual Properties*; King, R. B., Ed.; American Chemical Society: Washington, DC, 1976; Vol. 150, p 73.
(74) Neyhart, G. A.; Cheng, C. C.; Thorp, H. H. *J. Am. Chem. Soc.* **1995**, *117*, 1463.

Discussion

Impetus. The present study extends the earlier heteroleptic synthetic procedure for the preparation of complexes of the type $[Ru^{II}(bpy')(bpy'')(bpy''')]^{n+}$ in three important ways. The earlier procedure[53] was used exclusively in the preparation of tris(bidentate) complexes. There is a need in the coordination chemistry for more generality. Many recent studies based on ruthenium(II) polypyridyl complexes have relied on the functionalization of the Ru(II) center with a diverse array of ligands including terpyridines,[4,19,45,47,74−81] halides,[34,82] pseudohalides,[33,66,83−88] oxygen donors such as alkoxides or water,[45,68,89] sulfur donors,[90] and phosphorus donors.[34,91,92] A brief report of the use of heteroleptic bis(pyridine) complexes such as *cis*-$[Ru(bpy')(bpy'')(py)_2](PF_6)_2$ as synthetic intermediates was given by Rutherford et al.,[63] but a detailed investigation for the preparation of such complexes has not been reported. A procedure is described here for the preparation of such an example by using highly optimized reaction conditions. Also described is the preparation of heteroleptic isothiocyanate complexes of the type *cis*-$Ru^{II}(bpy')(bpy'')(NCS)_2$. This is notable because the incorporation of anions into the coordination spheres of the heteroleptic precursors *cis*-$[Ru(bpy')(bpy'')(CO)_2]^{2+}$ has proven difficult.

We also describe strategies for overcoming a limitation in the earlier procedure arising from the use of trimethylamine *N*-oxide (TMNO) as a decarbonylation reagent. TMNO is a potent oxygen atom transfer reagent and oxidizes many potential ligands. This has frustrated attempts to prepare heteroleptic chromophore−quencher complexes containing phenothiazine electron transfer donors or viologen electron-transfer acceptors in any reasonable yield for example.[63,93] It has also prevented application to phosphorus donor ligands because of their oxidation by TMNO to phosphine oxides. In previous work, *cis*-$[Ru(bpy')(bpy'')(py)_2]^{2+}$ has been used as a synthetic intermediate by pyridine replacement at high temperature. The acetonitrile intermediates developed here are more useful. They can be prepared under mild conditions in high yield and used under mild conditions in subsequent reactions.

We also describe here the preparation of highly functionalized ruthenium(II) polypyridyl complexes of the type *cis*-$[Ru^{II}(bpy')(bpy'')(X)(Y)]^{n+}$. Two approaches have been taken to these syntheses. In the first, the stepwise removal of the two carbonyl ligands from *cis*-$[Ru(bpy')(bpy'')(CO)_2]^{2+}$ gives first *cis*-$[Ru(bpy')(bpy'')(CO)(py)]^{2+}$ and, with a second equivalent of TMNO, *cis*-$[Ru^{II}(bpy')(bpy'')(py)(py')]^{2+}$. The second approach utilizes the earlier heteroleptic synthetic protocols and the reactivity of coordinated nitrosyls with azide to release N_2 and N_2O. Both methods were used independently in the preparation of the asymmetrical pyrazine-bridged complex *cis*,*cis*-$[((bpy)(tmb)(4\text{-}^tBupy)Ru)_2(pz)](PF_6)_4$.

Isothiocyanato Complexes. Interest in the use of pseudohalide complexes, particularly isothiocyanato complexes, has followed from the reports of their use as sensitizers of TiO_2 for photogalvanic applications.[13,15,55,94−100] The isothiocyanato complexes that have been used have been prepared by replacement of chloride in, for instance, *cis*-$Ru^{II}(4,4'\text{-}(COOEt)_2bpy)_2Cl_2$. We were interested in developing general procedures to heteroleptic bis(isothiocyanato)Ru^{II} dyes as a way of extending light absorptivity in the visible, for example.

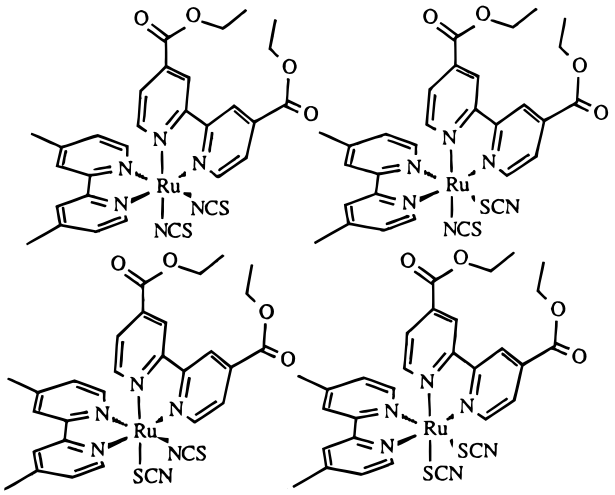
The precursor *cis*-$Ru^{II}(bpy)(dmb)Cl_2$ was prepared, but in very low yield, by reaction of *cis*-$[Ru(bpy)(dmb)(CO)_2](PF_6)_2$ with TMNO in refluxing 2-methoxyethanol for 24 h in the presence of a 100-fold excess of chloride. The major side product was incompletely reacted *cis*-$[Ru(bpy)(dmb)(CO)Cl]^+$. Attempts to prepare *cis*-$Ru(bpy)(tmb)(NO_2)_2$ were also frustrated by difficulties arising from removal of the second carbonyl ligand from *cis*-$[Ru(bpy)(tmb)(NO_2)(CO)](PF_6)_2$. The problem in these syntheses arises from addition of the first anionic ligand, which stabilizes the second carbonyl ligand toward reaction with TMNO. ν(CO) occurs at <1900 cm^{-1} in these complexes, indicating a significant weakening of the C−O bond. This weakening typically occurs via electron donation into the π^* antibonding orbital through a back-bonding interaction and is presumably accompanied by a concomitant strengthening of the Ru−C bond. Apparently, TMNO is not a sufficiently potent oxidant to overcome this effect in the case of complexes incorporating chloride. Similar attempts with other common decarbonylation reagents also proved difficult and inefficient.

The isothiocyanate anion is somewhat back-bonding, as shown by redox potential and infrared measurements. This decreases electron density at CO and allows further reaction with TMNO. Reaction of *cis*-$[Ru(dmb)(4,4'\text{-}(COOEt)_2bpy)(CO)_2](PF_6)_2$ with trimethylamine *N*-oxide in the presence of excess SCN^- in refluxing dimethoxyethane for 7 h led to isolation of *cis*-$Ru^{II}(dmb)(4,4'\text{-}(COOEt)_2bpy)(NCS)_2$ in 42% yield. The total yield for all the linkage isomers of this complex was even higher. This reaction appears to be completely general

(75) Kirchoff, J. R.; McMillan, D. R.; Marnot, P. A.; Sauvage, J. *J. Am. Chem. Soc.* **1985**, *107*, 1138.
(76) Grover, N.; Gupta, N.; Singh, P.; Thorp, H. H. *Inorg. Chem.* **1992**, *31*, 2014.
(77) Collin, J. P.; Guillerez, S.; Sauvage, J. P.; Barigelletti, F.; De Cola, L.; Flamigni, L.; Balzani, V. *Inorg. Chem.* **1991**, *30*, 4230.
(78) Collin, J. P.; Guillerez, S.; Sauvage, J. P. *J. Chem. Soc. Chem. Commun.* **1989**, 776.
(79) Cleary, R. L.; Byrom, K. J.; Bardwell, D. A.; Jeffery, J. C.; Ward, M. D.; Calogero, G.; Armaroli, N.; Flamigni, L.; Barigelletti, F. *Inorg. Chem.* **1997**, *36*, 2601.
(80) Beley, M.; Chodorowski, S.; Collin, J. P.; Sauvage, J. P.; Flamigni, J.; Barigelletti, F. *Inorg. Chem.* **1994**, *33*, 2543.
(81) Beley, M.; Collin, J. P.; Sauvage, J. P.; Sugihara, H.; Heisel, F.; Miehe, A. *J. Chem. Soc., Dalton. Trans.* **1991**, 3157.
(82) Cleare, M. J.; Griffith, W. P. *J. Chem. Soc. (A)* **1969**, 372.
(83) Coe, B. J.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1995**, *34*, 3600.
(84) Hatzidimitriou, A.; Gourdon, A.; Devillers, J.; Launnay, J.; Mena, E.; Amouyal, E. *Inorg. Chem.* **1996**, *35*, 2212.
(85) Rezvani, A. R.; Bensimon, C.; Cromp, B.; Reber, C.; Greedan, J. E.; Kondratiev, V. V.; Crutchley, R. J. *Inorg. Chem.* **1997**, *36*, 3322.
(86) Timpson, C. J.; Bignozzi, C. A.; Sullivan, B. P.; Kober, E. M.; Meyer, T. J. *J. Phys. Chem.* **1996**, *100*, 2915.
(87) Keene, F. R.; Salmon, D. J.; Walsh, J. L.; Abruña, H. D. *Inorg. Chem.* **1980**, *19*, 1896.
(88) Bignozzi, C. A.; Chiorboli, C.; Murtaza, Z.; Jones, W. E.; Meyer, T. J. *Inorg. Chem.* **1993**, *32*, 1036.
(89) Pinnick, D. V.; Durham, B. *Inorg. Chem.* **1984**, *23*, 1440.
(90) Root, M. J.; Sullivan, B. P.; Meyer, T. J.; Deutsch, E. *Inorg. Chem.* **1985**, *24*, 2731.
(91) Batista, A. A.; Polata, E. A.; Queiroz, S. L.; Otaciro, R. N.; James, B. R.; Rettig, S. J. *Inorg. Chim. Acta* **1995**, *230*, 111.
(92) Hudali, H. A.; Kingston, J. V.; Tayim, H. A. *Inorg. Chem.* **1979**, *18*, 1391.
(93) Treadway, J. A.; Chen, P.; Rutherford, T. J.; Keene, F. R.; Meyer, T. J. *J. Phys. Chem. A.* **1997**, *101*, 6824.
(94) Heimer, T. A.; Bignozzi, C. A.; Meyer, G. J. *J. Phys. Chem.* **1993**, *97*, 11987.
(95) Heimer, T. A.; Castellano, F. N.; Meyer, G. J. *Inorg. Chem.* **1994**, *33*, 5741.
(96) Heimer, T. A.; D'Arcangelis, S. T.; Farzad, F.; Stipkala, J. M.; Meyer, G. J. *Inorg. Chem.* **1996**, *35*, 5319.
(97) Argazzi, R.; Bignozzi, C. A.; Heimer, T. A.; Meyer, G. J. *Inorg. Chem.* **1997**, *36*, 2.
(98) Argazzi, R.; Bignozzi, C. *J. Am. Chem. Soc.* **1995**, *117*, 11815.
(99) Bignozzi, C. A.; Meyer, G. J.; Argazzi, R. *Inorg. Chem.* **1994**, *33*, 5741.
(100) Vlachopoulos, N.; Liska, P.; Augustynski, J.; Grätzel, M. *J. Am. Chem. Soc.* **1988**, *110*, 1216.

and the preparation of other heteroleptic bis(isothiocyanate) complexes is described elsewhere.[67,101]

Isomerism is an important aspect in the coordination chemistry of these complexes. The procedure used here led to all four of the possible isomers illustrated below. They were



separable chromatographically by utilizing a gradient elution from 0 to 25% (v/v) acetonitrile in toluene on a neutral alumina support. The first band was the major band and corresponded to the isomer in which both thiocyanate ligands are bound through nitrogen. This separation procedure, followed by a second chromatographic separation on silica gel with methanol as eluent allowed isolation of this isomer, as shown by ^{1}H NMR spectroscopy. This is in contrast to the report of Kohle et al.,[66] who found such a separation to be impossible. Perhaps the electronic asymmetry inherent in the heteroleptic complexes decreases thermal isomerization rates.

The ^{1}H NMR spectrum of *cis*-Ru(dmb)(4,4′-(COOEt)$_2$bpy)-(NCS)$_2$ in Figure 4 displays six sets of resonances in the alkyl region, two quartets (two protons each), two singlets (three protons each), and two triplets (three protons each). Since the isothiocyanate ligands are mutually cis in these complexes, all four rings of the bipyridyl ligands are inequivalent as are the four sets of substituents. The two singlets, therefore, correspond to the two methyl groups on dmb. One methyl is situated over a ring of the diester ligand and experiences the magnetic field from the ring currents induced by the external magnet. The second methyl is positioned over an isothiocyanate ligand, where there is no ring current effect. Similarly, one of the ethyl substituents of the 4,4′-(COOEt)$_2$bpy diester ligand experiences the ring currents from the dimethylbipyridine ligand and the other ethyl group is positioned over an isothiocyanate ligand. This leads to the splitting of the characteristic quartet and triplet peaks from the ethyl group into two sets of peaks. A similar one-to-one doubling of the peaks appears in the aromatic region of the spectrum.

The infrared spectrum of this complex (Table 1) is also indicative of structure. An intense ν(C═O) (ester) band appears at 1723 cm^{-1} and a ν(CN) band at 2100 cm^{-1} for the N-bound/N-bound linkage isomer. The absolute assignment of structure can only be made by obtaining X-ray crystallographic data or by preparing the complex with ^{13}C-enriched thiocyanate and comparing the chemical shift of the thiocyanate carbon in the ^{13}C NMR spectrum with known samples.[66,102,103]

Oxidation of the complex occurs at +0.73 V and a 4,4′-(COOEt)$_2$bpy-based reduction appears at −1.19 V (Table 3). A second, chemically irreversible oxidation, presumably accompanied by the production of thiocyanogen,[104,105] occurs at $E_{p,a}$ = +1.32 V. Scanning more reductively leads to a second chemically irreversible reduction at $E_{p,c}$ = −1.67 V, which is accompanied by loss of a thiocyanate ligand.[106] In the UV−visible absorbance spectrum, λ_{max} = 550 nm for the lowest lying MLCT band. It is red-shifted relative to comparable homoleptic complexes, as would be expected.[14,67,101]

Acetonitrile and Phosphine Complexes. By using previous synthetic procedures, it has not been possible to prepare heteroleptic complexes of ruthenium(II) containing phosphorus donor ligands because of oxidation of the ligands by trimethylamine *N*-oxide. To overcome this limitation, it was necessary to devise a synthetic intermediate which would allow the trimethylamine *N*-oxide and phosphine ligands to be added to the reaction in separate steps, and we developed *cis*-[Ru(bpy)-(tmb)(CH$_3$CN)$_2$](PF$_6$)$_2$ for this purpose. It was prepared by addition of 3 equiv of trimethylamine *N*-oxide (150% excess) to an acetonitrile solution of *cis*-[Ru(bpy)(tmb)(CO)$_2$](PF$_6$)$_2$ with heating at reflux for 1 h. Concentration of the reaction solution under reduced pressure and precipitation by addition of diethyl ether yielded the desired product sufficiently pure for most applications. Analytically pure material was obtained by chromatography on a short alumina column.

In the ^{1}H NMR spectrum (Figure 5), a striking pattern is observed. Six resonances of equal integration (three protons) corresponding to the four inequivalent methyl groups attached to the tetramethylbipyridine and the two inequivalent methyl groups in the acetonitrile ligands appear. The spectrum not only confirms the presence of acetonitrile, but also the expected cis configuration. Reaction of this complex at reflux in ethanol overnight in the presence of bis(diphenylphosphino)ethylene (dppe) led to nearly complete reaction, as determined by analytical HPLC by using cation-exchange resins as described in the Experimental Section.

To simplify investigations into the use of acetonitrile intermediates, the more symmetrical target [Ru(bpy)$_2$(dppe)](PF$_6$)$_2$ was chosen for investigation. Preparation of the acetonitrile intermediate required preparation of *cis*-[Ru(bpy)$_2$(CO)$_2$](PF$_6$)$_2$. This complex is remarkable in displaying no absorbance at wavelengths longer than 330 nm and no oxidations to +1.9 V due to strong back-bonding interactions between Ru and the CO ligands. The ^{1}H NMR spectrum of the phosphine complex matched the spectrum of the complex prepared by other methods.[34] The electrochemical and UV−visible properties of the complex agreed well with data previously reported.[34] The phosphine ligand is an exceptionally good back-bonding ligand as well in these complexes with $E_{1/2}^{III/II}$ = +1.69 V.

Pyridine Complexes. Acetone complexes have been used successfully as synthetic intermediates for the preparation of pyridyl complexes in previous work. We find that slow addition of trimethylamine *N*-oxide in acetone to a cold solution of carbonyl-containing precursor dramatically increases yields over

(101) Treadway, J. A. Creation and Utilization of Highly Unsymmetric Complexes of Ruthenium(II). Ph.D. Dissertation, University of North Carolina, Chapel Hill, NC, 1998.
(102) Kargol, J. A.; Crecely, R. W.; Burmeister, J. L. *Inorg. Chem.* **1979**, *18*, 2532.
(103) Kargol, J. A.; Crecely, R. W.; Burmeister, J. L. *Inorg. Chim. Acta* **1977**, *25*, L109.
(104) Golub, A.; Kolher, H.; Skopenko, V. V. *Chemistry of Pseudohalides*; Elsevier: New York, 1986.
(105) Newman, A. A. *The Chemistry and Biochemistry of Thiocyanic Acid and Its Derivatives*; Academic Press: New York, 1975.
(106) Sullivan, B. P.; Conrad, D.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 3640.

previous procedures. On the basis of solution infrared measurements, only one CO can generally be removed from *cis*-[Ru(bpy′)(bpy″)$(CO)_2$]$^{2+}$ at low temperature. This allows stepwise replacement of CO to form initially *cis*-[Ru(bpy′)(bpy″)(py)(CO)]$^{2+}$ and then *cis*-[Ru(bpy′)(bpy″)(py)(acetone)]$^{2+}$ without preparing the unstable bis(acetone) complex. A small amount of ligand scrambling (1%−3%) appears to occur during the course of this reaction. The overall isolated yields are ∼50% rather than ∼90% because of the difficulty in removing subtly different impurities such as these and [Ru(bpy′)(bpy″)$_2$]$^{2+}$. The decrease in yield is obviated when the materials are prepared on small scales, since the efficient HPLC techniques described above can be utilized preparatively.

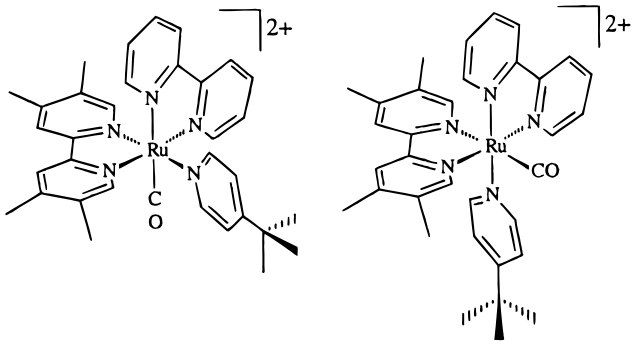
Several of these asymmetrical complexes have been prepared. The synthetic details and complete physical characterizations are reported elsewhere.[107] Included here are the details for the preparation and characterization of *cis*-[Ru(bpy)(dmb)(4-Etpy)$_2$]$(PF_6)_2$. The ^{1}H NMR spectrum for this complex is shown in Figure 2. The inequivalence of all six pyridyl rings in this complex is evident. The splitting of the methyl proton resonances in the dimethylbipyridine ligand into two singlets and of the methyl and methylene proton resonances from the 4-Etpy ligands into two triplets and two quartets is indicative of a cis geometry for the 4-Etpy ligands (the two quartets overlap with one of the singlets). The peak splitting is much smaller in this complex than in the acetonitrile or isothiocyanate complexes discussed above. The attenuation of the effect is a result of the relatively small magnetic differences between bipyridyl and pyridyl ligands compared, for example, to the differences between bipyridyl and isothiocyanate ligands.

The maximum for the lowest lying MLCT band (λ_{max} = 466 nm) is slightly red-shifted relative to that of the homoleptic parent complexes *cis*-[Ru(bpy)$_2$(4-Etpy)$_2$]$(PF_6)_2$ and *cis*-[Ru(dmb)$_2$(4-Etpy)$_2$]$(PF_6)_2$. The red shift is as expected given the arguments presented elsewhere.[14,67] The band arising from the MLCT transition to the pyridine ligand (λ_{max} = 429 nm) is also red-shifted relative to the parent complexes for the same reasons. In both cases, the electron-donating nature of the methyl groups in dimethylbipyridine stabilize the excited-state hole at *Ru^{III} and the lowest π* level at bpy is lower than at dmb. These effects appear in the electrochemical results in Table 3. The relationship between MLCT absorption band energies and the difference between metal oxidation and ligand reduction potentials has been documented elsewhere.[18,50,108−111]

Highly Asymmetrical Complexes. **Pyridine Carbonyls.** The procedures described here allow for the preparation of the highly functionalized, asymmetrical Ru^{II} complexes *cis*-[Ru^{II}(bpy′)(bpy″)(X)(Y)]$^{n+}$. One approach involved the stepwise replacement of CO in *cis*-[Ru(bpy′)(bpy″)$(CO)_2$]$(PF_6)_2$, and a second, the intermediates *cis*-[Ru(bpy′)(bpy″)(py)(NO)]$(PF_6)_2$ and their activation toward substitution by added azide anion (Scheme 3).

Preparation of *cis*-[Ru(bpy)(tmb)(CO)(4-^{t}Bupy)]$(PF_6)_2$ can be carried out at reflux in ethanol without significant loss of the second CO. To avoid didecarbonylation, a slight excess over 1 equiv of trimethylamine *N*-oxide was predissolved in ethanol and slowly dripped into the refluxing, deaerated solution of *cis*-[Ru(bpy)(tmb)$(CO)_2$]$(PF_6)_2$ and excess 4-^{t}Bupy over the course of 90 min. Loss of CO was followed by solution IR. At the end of the reaction period, a small amount of starting material remained, as shown by the appearance of bands of low intensity for ν(CO) at 2096 and 2041 cm^{-1} and the appearance of a new band at 1995 cm^{-1}. Additional TMNO was added to the reaction to complete the reaction.

The ^{1}H NMR spectrum of this complex (Figure 3) is remarkably resolved, especially given the low field strength (250 MHz) of the instrument. Ten resolved singlets are apparent in the region of the spectrum between 1.2 and 2.7 ppm, confirming the cis geometry of the pyridine and carbonyl ligands. As illustrated below, in these complexes there are two possible



geometrical isomers (see above). The asymmetry in the complex should lead to four singlet resonances between 2.0 and 3.0 ppm, one for each of the four sets of methyl protons in tetramethylbipyridine, and one singlet below 1.5 ppm, corresponding to the three sets of methyl protons from the *tert*-butyl substituent on the 4-^{t}Bupy ligand. Each should be doubled if both isomers are present and the doubling is indeed observed. From the intensity ratios, the isomers are present in a 1:1 ratio. As described above, the pattern of resonances is most likely the result of ring current effects.

Electronic asymmetry leading to large shifts due to inductive effects is possible but unlikely, given that no splitting was observed at 2 cm^{-1} resolution in the ν(CO) region in the infrared (Figure S3).

Back-bonding effects are obvious here. There is no oxidation wave for this complex to the solvent limit at +1.9 V. The lowest MLCT band appears at λ_{max} = 368 nm. The first ligand-based reduction occurs at −1.17 V, more anodic than the other complexes. Similarly, for *cis*-[Ru(bpy)(dmb)(CO)(4-^{t}Bupy)]$(PF_6)_2$ there is no wave for the $Ru^{III/II}$ couple and λ_{max} = 350 nm.

Pyridine Nitrosyls. *cis*-[Ru^{II}(bpy)(tmb)(4-^{t}Bupy)(NO)]$(PF_6)_3$ was prepared from *cis*-[Ru(bpy)(tmb)$(CO)_2$]$(PF_6)_2$ via *cis*-[Ru(bpy)(tmb)(4-^{t}Bupy)$_2$]$(PF_6)_2$ which was synthesized in situ and not purified. The crude bis(pyridine) was suspended in water and heated until most of the material had dissolved by forming *cis*-[Ru(bpy)(tmb)(4-^{t}Bupy)(H_2O)]$(PF_6)_2$. Addition of an acidic solution of sodium nitrite resulted in the immediate conversion of the aqua complex to the desired product. HPLC analysis of the crude product by cation exchange showed this material to be sufficiently pure for most purposes, suggesting that salts such as these should prove to be valuable synthetic intermediates in future studies. All detectable impurities were removed following two rapid recrystallizations from acetone/ether.

The nitrosyl complex displayed a reversible nitrosyl-based reduction at +0.48 V. A scan through the second nitrosyl-based reduction at $E_{p,c}$ = −0.42 V resulted in the appearance of new waves on the anodic scan at $E_{p,a}$ = −0.32, −0.18, and +0.68 V. Addition of excess azide to an acetone solution of *cis*-[Ru(bpy)(tmb)(4-^{t}Bupy)(NO)]$(PF_6)_3$ caused an immediate color change from pale yellow to dark purple. The nitrosyl stretch in the infrared spectrum at 1939 cm^{-1} was replaced with an azide

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stretch at 2036 cm^{-1}. Both the electrochemical response and the behavior displayed in the presence of excess azide anion appear to be typical of this class of complexes and parallel those displayed by homoleptic analogues.[57−62]

Dimers. The nitrosyl−azide reaction was also used to prepare *cis,cis*-[((bpy)(tmb)(4-^{t}Bupy)Ru)$_2$(pz)](PF$_6$)$_4$ from *cis*-[Ru(bpy)(tmb)(CO)$_2$](PF$_6$)$_2$ through the nitrosyl complex *cis*-[Ru(bpy)(tmb)(4-^{t}Bupy)(NO)](PF$_6$)$_2$. One equivalent of a methanolic solution of sodium azide was slowly added dropwise to an acetone solution of the nitrosyl complex under Ar. The addition was made slowly to avoid reaction of azide with the solvento complex. One-half equivalent of pyrazine dissolved in acetone was added and the reaction heated at reflux overnight.

The resulting ligand-bridged complex had one-electron oxidations at +1.25 and +1.37 V, consistent with weak electronic coupling across the pyrazine bridge. On negative scans a one-electron pyrazine-based reduction was observed at −1.03 V followed by a two-electron wave at −1.44 V corresponding to simultaneous reduction at bipyridine ligands on both sides of the bridge. A low-energy $Ru^{II} \rightarrow$ pz MLCT band appears at $\lambda_{max} = 498$ nm. In previous work on homoleptic analogues of this complex, both the 120 mV splitting in the metal-based couples and the 2:1 ratio in current intensities for the ligand reductions were observed.[112] The large red shift in the lowest energy MLCT absorption band is also characteristic of dimer formation across the pyrazine bridge.[112,113]

A simpler approach to the same complex but based on carbonyl ligand replacement in dicarbonyl precursors is illustrated in Scheme 3 (see also Figure 6). In this case, *cis*-[Ru(bpy)(tmb)(CO)$_2$](PF$_6$)$_2$ was dissolved in ethanol with 4-^{t}Bupy and heated at reflux with slightly greater than 1 equiv of trimethylamine *N*-oxide dissolved in ethanol added dropwise over the course of 90 min. When the reaction was complete, the solvent was removed and the residue triturated with ether to remove unreacted 4-^{t}Bupy. The ligand-bridged complex was formed by heating the residue in 2-methoxyethanol at reflux in the presence of 0.5 equiv of pyrazine and 1 equiv of TMNO. Physical characterization of this material showed it to be identical to that obtained by the nitrosyl route.

This latter procedure has the advantage of being significantly easier to carry out and can be used whenever both halves of the ligand-bridged complex are the same. Whichever method is employed, the most significant impurities in the isolated crude material were dicationic, whereas the desired product was a tetracation. Cation-exchange chromatography was particularly effective for the purification of the ligand-bridged complexes.

Conclusions

Impressive progress has been made in the ~20 years since the early synthetic advances based on the early work by Dwyer et al. in the field of Ru^{II} polypyridyl chemistry were first published.[35,36] The methodology depicted in Scheme 2 represented an important milestone since it greatly increased the number of synthetic possibilities open to a given ligand set. Here, we have described strategies which build upon and enhance this methodology to two useful ends. The generality is extended to include combinations of ligands which were inaccessible or accessible only with difficulty. The number of different ligands which can be incorporated into a single complex has been extended impressively. The result is a rich, versatile synthetic framework which is quite general.

Where possible, redundancy has been built into the synthesis in order to ensure maximum generality by providing multiple pathways to most targets. For instance, the acetonitrile complexes are attractive intermediates, but higher yields are often attainable by using acetone complexes as intermediates. Similarly, nitrosyl intermediates provide a route to highly functionalized ligand-bridged complexes, but selective CO removal is simpler for complexes which are symmetrical across the bridge.

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Supporting Information Available: ^{1}H NMR spectrum of [Ru(bpy)(tmb)(dppe)](PF$_6$)$_2$ and the dppe ligand in dichloromethane-d_2; IR spectra of *cis*-[Ru(bpy)(tmb)(CO)$_2$](PF$_6$)$_2$, *cis*-[Ru(bpy)(tmb)(4-^{t}Bupy)(CO)](PF$_6$)$_2$, *cis*-[Ru(bpy)(tmb)(4-^{t}Bupy)(NO)](PF$_6$)$_3$, *cis*-[Ru(bpy)(tmb)(CH$_3$CN)$_2$](PF$_6$)$_2$, and *cis*-*N*,*N*-Ru(dmb)(4,4′-(COOEt)$_2$bpy)(NCS)$_2$; and cyclic voltammograms of *cis*-*N*,*N*-Ru(dmb)(4,4′-(COOEt)$_2$bpy)(NCS)$_2$, *cis*-[Ru(bpy)(tmb)(CO)(4-^{t}Bupy)]$^{2+}$, *cis*-[Ru(bpy)(tmb)(CH$_3$CN)$_2$]$^{2+}$, [Ru(bpy)(tmb)(dppe)]$^{2+}$, and *cis*-[Ru(bpy)(tmb)(4-^{t}Bupy)(NO)]$^{3+}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(108) Ohsawa, Y.; Hanck, K. W.; DeArmond, M. K. *J. Electroanal. Chem.* **1984**, *175*, 229.
(109) Dodsworth, E. S.; Vlcek, A. A.; Lever, A. B. P. *Inorg. Chem.* **1994**, *33*, 1045.
(110) Ghosh, P.; Chakravorty, A. *Inorg. Chem.* **1984**, *23*, 2242.
(111) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617.
(112) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1289.
(113) Veletsky, N. I.; Dementiev, I. A.; Ershov, A. Y.; Nikol'skii, A. B. *J. Photochem. Photobiol.* **1995**, *89*, 99.