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Steric Ligand Effects of Six Bidentate Bipyridyl Ligands

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The synthesis and characterization of a series of $[Ru(H_2O)(N\text{-}N)(trpy)]^{2+}$ complexes (where N-N = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 4,7-dimethyl-1,10-phenanthroline (4,7-Me_2phen), 2,9-dimethyl-1,10-phenanthroline (2,9-Me_2phen), 2,2′-biquinoline (biq), and 6,6′-dichloro-2,2′-bipyridine (6,6′-Cl_2bpy), and trpy = 2,2′:6′,2″-terpyridine) are described. The rate constants for ligand substitution of the aqua ligand for acetonitrile were determined for the $[Ru(H_2O)(N\text{-}N)(trpy)]^{2+}$ complexes as well as for a series of $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ complexes in pH = 2.2 $HNO_3/NaNO_3$ ($\mu = 0.1$) solution at 25 °C. The electronic (E) and steric (S) properties of the phopshine ligands in the $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ complexes correlated well with the rate constants for ligand substitution (k_{ls}) using the relationship $\ln k_{ls} = aE + bS + c$ (where a–c are constants which were determined by linear regression analyses). The equation for the $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ complexes was used to calculate the cone angles of the six bidentate bipyridyl ligands (N-N). These cone angles represent the first quantitative estimates of steric ligand effects for bidentate bipyridyl ligands.

Introduction

The ligand environment of transition metal coordination complexes can exert a profound influence on the stability and reactivity of transition metal centers.[2] In general, ligand influence can be considered in terms of electronic and steric ligand effects.[3–9] There have been a number of studies which concern electronic ligand effects, where some of the parameters used to describe electronic ligand effects include the chemical shifts (δ) and coupling constants (J) of the ligands,[10] equilibrium constants for the ionization of the acid form of the ligands,[11] the A_1 carbonyl stretching frequency of $Ni(CO)_3PR_3$ complexes,[12,13] and the redox potentials of the complexes.[14] Notably, there are far fewer studies involving the quantification of steric ligand effects.

Tolman[13] and Brown[8] have introduced quantitative values associated with the steric size of ligands. Tolman utilized cone angle values as a means of comparing the steric properties of monodentate tertiary phosphine ligands. Cone angles are useful measures of the steric size of the tertiary phosphine ligand, as demonstrated by good linear free energy correlations with a number of parameters, including the rate constants of hydrogenation,[15] the rate constants of ligand substitution,[16,17] and equilibrium data.[18] Recently, Brown introduced ligand repulsive energy, E_R, as a new measure of ligand steric effects based on molecular mechanics calculations.[8] E_R is defined as the repulsive force between a phosphine ligand and a $Cr(CO)_5$ metal center, arising solely from the van der Waals repulsive forces acting along the Cr–P bond axis. The correlation coefficients, r, from the application of $(f(x)) = aE + bS + c$ ($f(x)$ = a quantifiable reaction property such as a rate constant for ligand substitution, E = electronic parameter, S = steric parameter, and a–c are constants for a given reaction) were given when S was either Tolman's cone angle, θ, or Brown's ligand repulsive energy, E_R. Of the 35 reactions that were listed by Brown, 17 had a better correlation with θ as the steric parameter, 16 reactions had a better correlation with E_R as the steric parameter, and 2 had equal correlation coefficients.[8]

Bidentate bipyridyl ligands (such as 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen)) are often used in combination with transition metals and have great utility in the design of stoichiometric[19] and catalytic oxidants,[20–23] photochemical re-

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(1) (a) State University of New York at Buffalo. (b) The Pennsylvania State University at Erie.

(2) (a) Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds. *Comprehensive Coordination Chemistry*; Pergamon Press: New York, 1987. (b) Bell, C. F. *Principles and Applications of Metal Chelation*; Oxford University Press: Oxford, U.K., 1977.

(3) (a) Rahman, M. M.; Liu, H. Y.; Prock, A. P.; Giering, W. P. *Organometallics* **1987**, *6*, 650–658. (b) Eriks, K.; Giering, W. P.; Liu, H.-Y.; Prock, A. *Inorg. Chem.* **1989**, *28*, 1759–1765. (c) Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981–1991.

(4) Romeo, R.; Arena, G.; Scolaro, L. M. *Inorg. Chem.* **1992**, *31*, 4879–4884.

(5) Zizelman, P. M.; Amatore, C.; Kochi, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 3771–3784.

(6) (a) Xing-Fu, L.; Tian-Gi, S.; Ao-Ling, G.; Guang-Li, S.; Peng-Nian, S. *Inorg. Chim. Acta* **1987**, *129*, 227–234. (b) Xing-Fu, L.; Tian-Gi, S.; Ao-Ling, G.; Guang-Li, S.; Peng-Nian, S. *Inorg. Chim. Acta* **1987**, *129*, 235–244. (c) Xing-Fu, L.; Peng-Nian, S.; Ao-Ling, G.; Jing-Ci, L. *Inorg. Chim. Acta* **1987**, *129*, 245–252.

(7) Berger, R.; Schenkluhn, H.; Weimann, B. *Transition Met. Chem. (London)* **1981**, *6*, 277–287.

(8) Brown, T. L. *Inorg. Chem.* **1992**, *31*, 1286–1294 and references therein.

(9) Chen, L.; Poe, A. J. *Inorg. Chem.* **1989**, *28*, 3641–3647.

(10) (a) Allman, T.; Goel, R. G. *Can. J. Chem.* **1982**, *60*, 716–722. (b) Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951–1958.

(11) (a) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195 and references therein. (b) Mastryukova, T. A.; Kabachnik, M. I. *Russ. Chem. Rev. (Engl. Transl.)* **1969**, *38*, 795–811.

(12) Bartik, T.; Himmler, T.; Schulte, H.-G.; Seevogel, K. *J. Organomet. Chem.* **1984**, *272*, 29–41.

(13) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.

(14) (a) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271–1285. (b) Lever, A. B. P. *Inorg. Chem.* **1991**, *30*, 1980–1985.

(15) Montelactici, S.; van der Ent, A.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 1054–1060.

(16) Connor, J. A.; Riley, P. I. *J. Organomet. Chem.* **1975**, *94*, 55–60.

(17) Halpern, J.; Phelan, P. F. *J. Am. Chem. Soc.* **1972**, *94*, 1881–1886.

(18) Fischer, H.; Fischer, E. O. *Chem. Ber.* **1974**, *107*, 673–679.

(19) (a) Marmion, M. E.; Takeuchi, K. J. *J. Am. Chem. Soc.* **1988**, *110*, 1472–1480. (b) Acquaye, J. H.; Muller, J. G.; Takeuchi, K. J. *Inorg. Chem.* **1993**, *32*, 160–165. (c) Muller, J. G.; Acquaye, J. H.; Takeuchi, K. J. *Inorg. Chem.* **1992**, *31*, 4552–4557. (d) Kubow, S. A.; Marmion, M. E.; Takeuchi, K. J. *Inorg. Chem.* **1988**, *27*, 2761–2767.

(20) (a) Cabaniss, G. E.; Diamantis, A. A.; Murphy, W. R., Jr.; Linton, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 1845–1853. (b) Kutner, W.; Meyer, T. J.; Murray, R. W. *J. Electroanal. Chem. Interfacial Electrochem.* **1985**, *195*, 375–394.

(21) (a) Che, C. M.; Leung, W.-H.; Poon, C.-K. *J. Chem. Soc., Chem. Commun.* **1987**, 173–175. (b) Che, C.-M.; Ho, C.; Lau, T.-C. *J. Chem. Soc., Dalton Trans.* **1991**, 1901–1907.

(22) Bailey, C. L.; Drago, R. S. *J. Chem. Soc., Chem. Commun.* **1987**, 179–180.

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agents,[24] and complexation reactions.[2] Cundari and Drago,[25] Che,[21] and others[26] suggested that the steric effects of ligands in the primary coordination sphere of high-oxidation-state transition metals may control product yields and product distributions in the oxidation of organic substrates by transition metal complexes. Thus the quantitative evaluation of the steric ligand effects of polypyridine ligands is potentially of importance in the general design of transition metal mediated electron-transfer processes. Although the steric ligand effects of tertiary phosphine ligands have been quantified by Tolman,[13] Brown,[8] and others,[9,27,28] the steric ligand effects of bipyridyl ligands have been studied only qualitatively; our literature search has shown that there is no common method for determining and comparing the steric ligand effects of bidentate bipyridyl ligands. Our present study focuses on six commonly used bidentate bipyridyl ligands, namely bpy, phen, 2,9-dimethyl-1,10-phenanthroline (2,9-Me_2Phen), 4,7-dimethyl-1,10-phenanthroline (4,7-Me_2phen), 2,2'-biquinoline (biq), and 6,6'-dichloro-2,2'-bipyridine (6,6'-Cl_2bpy).

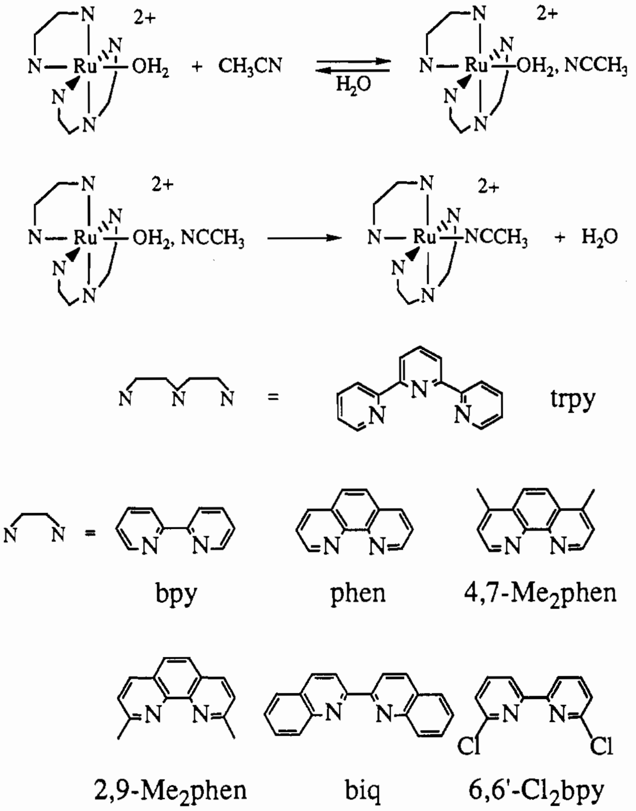
Previously, we reported that the log values of the rate constants of ligand substitution for $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ complexes correlate well with the reported cone angle values for the tertiary phosphine ligands (PR_3).[29] With this paper, we will extend our original ligand substitution studies to include complexes which have bidentate ligands. First, a family of complexes of the form $[Ru(H_2O)(N\text{-}N)(trpy)]^{2+}$ (where trpy = 2,2':6',2''-terpyridine; N-N = bpy, phen, 4,7-Me_2phen, 2,9-Me_2phen, biq, and 6,6'-Cl_2bpy) were prepared and the rate constants of ligand substitution (see Scheme I) were measured. Second, the electronic (*E*) and steric (*S*) properties of the phosphine ligands in the $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ complexes were correlated with the rate constants for ligand substitution (k_{ls}) using the relationship $\ln k_{ls} = aE + bS + c$ (where *a*–*c* are constants which were determined by linear regression analyses). Finally, the equation for the $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ complexes was used to calculate the cone angles of the six bidentate bipyridyl ligands (N-N). These cone angles represent the first quantitative estimates of steric ligand effects for bidentate bipyridyl ligands.

Experimental Section

Materials. All chemicals were of reagent grade and were used without further purification unless otherwise noted. $NaBF_4$ was partially dissolved in distilled water (5 g/10 mL), and the mixture was filtered before use to remove impurities. Acetonitrile, obtained from Fisher Scientific, was fractionally distilled over CaH_2 and stored over 3-Å sieves. House-distilled water was passed through a Barnstead combination cartridge and an organic removal cartridge before use. All kinetics measurements were performed using 6.8×10^{-3} M HNO_3 (pH = 2.2) with $NaNO_3$ added to increase the ionic strength (μ) to 0.1 M. Nitromethane was fractionally distilled over $CaCl_2$ (5% w/v) prior to use.

Measurements. Electronic absorption spectra were recorded with a Milton Roy Spectronic 3000 diode array spectrophotometer equipped with a Hewlett Packard 7470A plotter or with a Bausch and Lomb Spectronic 2000 spectrophotometer equipped with a Houston Instruments Model 200 recorder. Electrochemical experiments were carried out in a three-electrode, one-compartment cell equipped with a platinum disk (nonaqueous solutions) or glassy carbon (aqueous solutions) working electrode, a platinum wire auxiliary electrode, and a saturated sodium chloride calomel reference electrode (SSCE) using an IBM EC/225 polarographic analyzer equipped with a Houston Instruments Model 100 recorder. Nonaqueous electrochemistry was conducted with methylene chloride as the solvent and 0.1 M tetrabutylammonium tetrafluoroborate (TBAB) as the supporting electrolyte. Aqueous electrochemistry was conducted with $\mu = 0.1$ M solution (phosphate, sulfate, or nitrate) at the appropriate pH in a constant-temperature bath at 25 °C. pH measurements and pK_a determinations were conducted using an Orion Research Digital Ionalyzer, Model 501. Infrared spectra of Nujol mulls on NaCl plates were recorded with a Perkin-Elmer 1430 ratio-recording IR spectrophotometer. Kinetics studies were conducted using Beckman DU spectrophotometers that were retrofitted with Gilford accessories. In general, solutions were maintained at constant temperature by the circulation of water from a thermostated water bath. Elemental analyses were performed by Atlantic Microlabs (Norcross, GA). Linear regression analyses were computed using the SigmaPlot Scientific Graph System 4.14 for the Macintosh by Jandell Scientific. The tolerance level for these calculations was 1×10^{-7}.

Scheme I. Reactions of $[Ru(H_2O)(N\text{-}N)(trpy)]^{2+}$ Complexes with Acetonitrile



Kinetics Procedure. The kinetics of acetonitrile ligand substitution of the ruthenium(II) complexes were conducted in pH = 2.2, $HNO_3/NaNO_3$, $\mu = 0.1$ M at 25 °C. In a typical kinetics experiment, the reaction was initiated by adding 2 mL of the solution containing the metal complex (typically 2.0×10^{-4} M) to 1 mL of one of eight solutions of varying concentrations of the incoming ligand, acetonitrile (typically 0.2–2.5 M). Both solutions were thermally equilibrated and then mixed quickly in the cell with a disposable pipet. The absorbance versus time curve was recorded with the use of a calibrated chart drive as a time base.

pK_a Determinations. The pK_a values of the protonated form of the ligands biq and 6,6'-Cl_2bpy were determined by following the method of Streuli, which was developed for the titration of aqueous bases and water-insoluble phosphines.[30] Each of the ligands was dissolved in nitromethane to a concentration of 2.5×10^{-3} M before titrating against a solution of $HClO_4$ in nitromethane. All titration curves were plotted as potential (mV) versus amount (mL) of acid added. The half-equivalence point of each titration (half-neutralization potential, HNP) was then plotted against reported pK_a values for the protonated forms of the ligands: bpy,

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(23) (a) Leising, R. A.; Takeuchi, K. J. *Inorg. Chem.* **1987**, *26*, 4391–4393. (b) Bessel, C. A.; Leising, R. A.; Takeuchi, K. J. *J. Chem. Soc., Chem. Commun.* **1991**, 833–835.

(24) (a) Thummel, R. P.; Lefoulon, R. *Inorg. Chem.* **1987**, *26*, 675, 2370–2376. (b) Thummel, R. P.; Lefoulon, F.; Chirayil, S. *Inorg. Chem.* **1987**, *26*, 3073–3074. (c) Sandrini, D.; Maesti, M.; Belser, P.; von Zelewsky, A.; Balzani, V. *J. Phys. Chem.* **1985**, *89*, 3675–3679. (d) Krause, R. A. *Struct. Bonding* **1987**, *67*, 1. (e) Balzani, V. *Photochemistry of Coordination Compounds*; Academic Press: London, 1970.

(25) Cundari, T. R.; Drago, R. S. *Inorg. Chem.* **1990**, *29*, 487–493.

(26) Groves, J. T.; Quinn, R. *J. Am. Chem. Soc.* **1985**, *107*, 5790.

(27) DeSanto, J. T.; Mosbo, J. A.; Storhoff, B. N.; Bock, P. L.; Bloss, R. E. *Inorg. Chem.* **1980**, *19*, 3086–3092.

(28) Ferguson, G.; Roberts, P. J.; Alyea, E. C.; Khan, M. *Inorg. Chem.* **1978**, *17*, 2965–2967.

(29) Leising, R. A.; Ohman, J. S.; Takeuchi, K. J. *Inorg. Chem.* **1988**, *27*, 3804–3809.

(30) (a) Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985–987. (b) Henderson, W. A.; Streuli, C. A. *J. Am. Chem. Soc.* **1960**, *82*, 5791–5794.

phen, 2,9-Me_2phen and 4,7-Me_2phen, pyridine, 2-bromopyridine, 2-fluoropyridine, 2-methylpyridine, and 2,6-dimethylpyridine in aqueous solutions[31] (HNP = $-62.79(pK_a) + 538.35$ $R^2 = 0.98$) so that the pK_a values of the protonated forms of biq and 6,6′-Cl_2bpy could be determined by extrapolation. The calculated pK_a value for the protonated form of 6,6′-Cl_2bpy is -0.154, and that for biq is 3.32. This procedure was necessary, as the solubility of 6,6′-Cl_2bpy was very low in aqueous solutions and the pK_a for biq in aqueous solutions has not been reported.

Preparations. The $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ complexes were prepared as reported in the literature.[19] Literature procedures were used to prepare trpy,[32] 6,6′-Cl_2bpy,[33] and $Ru(Cl)_3$(trpy).[34] $[Ru(bpy)(Cl)(trpy)]^{2+}$ (**1**) and $[Ru(H_2O)(bpy)(trpy)]^{2+}$ (**7**) were prepared as reported by Meyer and co-workers,[35] and $[Ru(Cl)(6,6'\text{-}Cl_2bpy)(trpy)]^{2+}$ (**12**) were prepared by a modification of the Che synthesis.[21]

[Ru(Cl)(phen)(trpy)](BF_4)·0.5H_2O (2). $Ru(Cl)_3$(trpy) (200 mg, 0.45 mmol), 1 equiv of phen (81 mg, 0.45 mol), and 0.02 g (0.47 mmol) of LiCl were combined before adding 40 mL of 75% EtOH/25% H_2O. The mixture was outgassed for 5 min with $N_2(g)$, 0.1 mL of the reductant, Et_3N was added, and the reaction was heated to reflux for 4 h. After reaction, the mixture was filtered hot through a medium frit. A solution of $NaBF_4$ (1.0 g in 5 mL of distilled H_2O) was added, and the solution was stored in a refrigerator overnight. The next day, the solution was again filtered to remove insoluble bypyroducts, the filtrate was reduced to a volume of ca. 10 mL, and the solid was filtered off and dried in a vacuum oven. The sample, dissolved in 10% MeOH/90% CH_2Cl_2, was passed down an alumina column, where the initial orange-red band was collected. An equal volume of toluene was added, and the volume of the solution was reduced. The solid was filtered off, washed with toluene, and air-dried. Yield 53%. Anal. Calcd for $C_{27}H_{19}N_5ClBF_4Ru\cdot0.5H_2O$: C, 50.22; H, 3.12. Found: C, 49.99; H, 2.93.

[Ru(Cl)(4,7-Me_2phen)(trpy)](BF_4)·2.5H_2O (3). The synthetic procedure of **2** was followed however the solvent was 95% ethanol and the reaction was allowed to reflux for 8 hours under $N_2(g)$. The reaction was filtered through a medium frit while hot to remove a small amount of insoluble material. The red-brown solution was chilled in the refrigerator overnight and again filtered through a medium frit. A solution of $NaBF_4$ (5 g/10 mL H_2O) was added causing immediate precipitation of needle-like brown crystals. These crystals were filtered, washed with cold H_2O and air dried. The compound was purified by redissolving in CH_2Cl_2 and filtering any insoluble impurities. Yield: 98%. Anal. Calcd for $C_{29}H_{23}N_5ClBF_4Ru\cdot2.5H_2O$: C, 49.07; H, 3.98. Found: C, 48.78; H, 3.54.

[Ru(Cl)(2,9-Me_2phen)(trpy)](BF_4)·0.5H_2O (4). The synthetic procedure and purification was the same as that of **2**. Careful column chromatography (alumina with 2–5% MeOH/CH_2Cl_2) was required to purify the sample. The product eluted as the initial red-brown band from the column. An equal volume of toluene was added, and the volume was reduced slowly using a rotary evaporator. The product, a red-brown solid, was collected by vacuum filtration, washed with toluene, and air-dried. Yield: 10%. Anal. Calcd for $C_{29}H_{23}N_5ClBF_4Ru\cdot0.5H_2O$: C, 51.69; H, 3.58. Found: C, 51.94; H, 3.83.

[Ru(biq)(Cl)(trpy)](BF_4)$_2$·0.25C_6H_{14} (5). The synthetic procedure and purification followed the method for complex **4**. The initial dark purple-blue band was collected. Yield: 63%. Anal. Calcd for $C_{33}H_{23}N_5ClBF_4Ru\cdot0.25C_6H_{14}$: C, 56.41; H, 3.64. Found: C, 56.46; H, 3.82.

[Ru(H_2O)(phen)(trpy)](BF_4)$_2$·0.5H_2O (8). The procedure was the same as that used to synthesize **7**. Yield: 60%. ^1H NMR (CD_3CN (ppm)): 7.1–10.0 (m, aromatic protons). Anal. Calcd for $C_{27}H_{21}N_5OB_2F_8Ru\cdot0.5H_2O$: C, 45.92; H, 3.00. Found: C, 46.04; H, 2.95.

[Ru(H_2O)(4,7-Me_2phen)(trpy)](BF_4)$_2$·2H_2O (9). A 0.52-g sample (7.9×10^{-4} mol) of **1** was dissolved in 50 mL of acetone and 19 mL of distilled H_2O. $AgBF_4$ (0.24 g, 1.6 equiv) was added, and the reaction mixture was refluxed under $N_2(g)$ for 1 h. After being cooled to room temperature, the mixture was filtered through a fine frit to remove AgCl and the solution was chilled in the refrigerator overnight. The reaction mixture was again filtered to remove any remaining starting materials, and the volume was slowly reduced to ca. 10 mL on a rotary evaporator. The microcrystalline brown precipitate was filtered off, washed with a minimal amount of cold H_2O, and air-dried. Yield: 34%. ^1H NMR (CD_3CN (ppm)): 7.2–9.8 (m, aromatic protons, 17H), 3.15 (s, CH_3, 3H), 2.75 (s, CH_3, 3H). Anal. Calcd for $C_{29}H_{25}N_5OB_2F_8Ru\cdot2H_2O$: C, 45.22; H, 3.80. Found: C, 45.30; H, 3.78.

Table I. Second-Order Rate Constants for the Exchange of the Water Ligand with Acetonitrile for $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ Complexes, pK_a Values for the Protonated Forms of the Phosphine Ligands, Cone Angles, and E_R Values for the Phosphine Ligands

PR_3[a]	10^4k (M^{-1} s^{-1})[b]	pK_a[c]	θ (deg)[d]	E_R[e]
PMe_3	0.31	8.65	118	39
PEt_3	2.0	8.69	132	61
$P(n\text{-}Pr)_3$	5.1	8.64	132	
$P(n\text{-}Bu)_3$	7.1	8.43	132	64
$P(i\text{-}Pr)_3$	300		160	109
PCy_3	990	9.65	170	116
$P(p\text{-}C_6H_4F)_3$	4.3	1.97	145	74
$P(C_6H_5)_3$	11	2.73	145	75
$P(p\text{-}C_6H_4CH_3)_3$	20	3.84	145	74
$P(p\text{-}C_6H_4OCH_3)_3$	15	4.57	145	76

[a] Abbreviations used for phosphine substituents: Me = methyl, Et = ethyl, Pr = propyl, Bu = butyl, Cy = cyclohexyl, p-C_6H_4F = p-fluorophenyl, C_6H_5 = phenyl, p-$C_6H_4CH_3$ = p-tolyl, p-$C_6H_4OCH_3$ = p-methoxyphenyl. [b] pH = 2.2 $HNO_3/NaNO_3$ (μ = 0.1 M) at 25 °C. [c] pK_a values were taken from ref 30. [d] Cone angles were taken ref 13. [e] E_R values were taken from ref 8.

[Ru(H_2O)(2,9-Me_2phen)(trpy)](BF_4)$_2$·2H_2O (10). The procedure was the same as that used to synthesize **9**. Yield: 40%. ^1H NMR (CD_3CN (ppm)): 7.2–8.9 (m, aromatic protons, 17H), 3.22 (s, CH_3, 3H), 1.75 (s, CH_3, 3H). Anal. Calcd for $C_{29}H_{25}N_5OB_2F_8Ru\cdot2H_2O$: C, 45.22; H, 3.80. Found: C, 45.58; H, 3.81.

[Ru(H_2O)(biq)(trpy)](BF_4)$_2$·2H_2O (11). The procedure was the same as that used to synthesize **9**; however, recrystallization from H_2O (5 mg of **11**/mL of H_2O) was required to purify the sample. Yield: 49%. ^1H NMR (CD_3CN (ppm)): 6.7–9.0 (m, aromatic protons). Anal. Calcd for $C_{33}H_{25}N_5OB_2F_8Ru\cdot2H_2O$: C, 48.43; H, 3.57. Found: C, 48.09; H, 3.52.

Results

The ligand substitution reactions were monitored spectrophotometrically for all of the aquaruthenium(II) complexes. The decrease in the wavelength maximum corresponding to the MLCT band of the initial aquaruthenium(II) complex was used for the $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ complexes. Pseudo-first-order conditions were employed, where the incoming acetonitrile was in excess (≥100 equiv). The spectra corresponding to the substitution reactions were found to proceed isosbestically in each case. Plots of $\ln[(A_0 - A_\infty)/(A_t - A_\infty)]$ versus time were linear, and the pseudo-first-order rate constants were calculated by using an iterative least-squares curve-fitting analysis of the rate data according to eq 1, where A_∞ is the absorbance at the completion

$$\ln[(A_0 - A_\infty)/(A - A_\infty)] = k_{obs}t \qquad (1)$$

of the substitution reaction, A_0 is the initial absorbance, A is the absorbance measured at time t, and k_{obs} is the pseudo-first-order rate constant. The rate constant for ligand substitution, k, was then calculated by using an iterative least-squares curve-fitting analysis of the equation $k = k_{obs}/[CH_3CN]$.

The substitution of the aqua ligand by acetonitrile in the $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ complexes was carried out in aqueous solution (pH = 2.2 $HNO_3/NaNO_3$, μ = 0.1 M), and the results are presented in Table I. Our earlier studies[29] demonstrated that these complexes undergo a dissociative interchange mechanism for ligand substitution, as expected for octahedral ruthenium(II) centers.[36,37] The increase in the wavelength maximum

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(31) Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*; Butterworths: London, 1965.

(32) Jameson, D. L.; Guise, L. E. *Tetrahedron Lett.* **1991**, *32*, 1999–2002.

(33) Ogawa, S.; Shiraishi, S. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2527–2530.

(34) Leising, R. A.; Kubow, S. A.; Churchill, M. R.; Buttrey, L. A.; Ziller, J. W.; Takeuchi, K. J. *Inorg. Chem.* **1990**, *29*, 1306–1312.

(35) Takuchi, K. J.; Thompson, M. S.; Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 1845–1951.

(36) Taube, H. *Comments Inorg. Chem.* **1981**, *1*, 17–31.

(37) Swaddle, T. W. *Coord. Chem. Rev.* **1974**, *14*, 217–268.

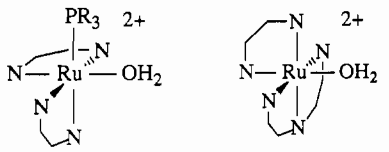

Figure 1. Comparison of the structures of $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ and $[Ru(H_2O)(N\text{-}N)(trpy)]^{2+}$.

corresponding to the MLCT band of the final (acetonitrile)ruthenium(II) complex was used to study the substitution of the aqua ligand in the $[Ru(H_2O)(N\text{-}N)(trpy)]^{2+}$ complexes. The rate data were obtained and analyzed in a manner similar to the procedure outlined above for the $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ complexes. The precision of the measurements for all of the second-order rate constants was within 10% at the 95% confidence limit.

Discussion

Previously, we studied the ligand substitution chemistry of the $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ family of complexes and discovered a linear relationship between the log values of the rate constants of ligand substitution and the reported cone angle values for the tertiary phosphine ligands (PR_3).[29] From our success with this study, we were optimistic for several reasons that the ligand substitution kinetics for $[Ru(H_2O(N\text{-}N)(trpy)]^{2+}$ complexes could be combined with our kinetics data for $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ complexes to generate cone angles for bidentate ligands. First, the mechanism of ligand substitution reactions at six-coordinate ruthenium(II) centers was well characterized by Taube[36] and others[29,37] as a dissociative interchange mechanism (I_d), where the rate-determining step involves the loss of the leaving group from the encounter complex (see Scheme I). Second, for all of the ruthenium complexes studied, the spectator ligands remain firmly bonded to the ruthenium center and only the aqua ligand is involved in the ligand substitution process. Third, the magnitudes of the rate constants of ligand exchange allowed the use of conventional mixing techniques and yet inconveniently long reaction times were avoided. Fourth, the structural similarities between the $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ and $[Ru(H_2O)(N\text{-}N)(trpy)]^{2+}$ families of complexes (Figure 1) suggest that the rate constants of ligand substitution will be most influenced by the steric properties of the substituents in the cis position relative to the aqua ligand and thus these influences should be comparable.

Since both the electronic and steric properties of a ligand must be considered to accurately describe the ligand effects on ligand substitution at a ruthenium(II) center, we needed a method to quantitatively separate the electronic ligand effects from the steric ligand effects in order to determine the size of the bidentate ligands of interest. In general, the electronic and steric ligand effects on transition metal reactivity have been studied by several research groups.[3-9] The general equation (2) was used to describe

$$f(x) = aE + bS + c \qquad (2)$$

the contributions of the electronic (E) and steric (S) ligand effects to the reactivity of a complex ($f(x)$).[3,7,38] The electronic and steric parameters were weighted by the use of constants a and b, which give an indication of the relative importance of the electronic and steric contributions to the reaction. For our studies, the sign of the a coefficient indicated whether the transition state is electron-demanding or electron-releasing relative to the ground state. The sign of the b coefficient indicated whether an increasing steric requirement of the ligand impedes or accelerates the reaction. The calculated percentage of the electronic influence is defined as the calculated range of {the electronic contributions (at the smallest steric contribution)}/{the calculated range of the electronic contribution (at the smallest steric contribution) + the calculated range of the steric contribution (at the smallest electronic contribution)}.[7] The calculated percentages or ratios enable a comparison of the significance of the electronic and steric contributions even though the means of describing the electronic or steric terms may differ, depending on the available data.[37,38] Finally, the correlation coefficients of the plot of ln $(k_{ls})_{calc}$ vs ln $(k_{ls})_{exp}$ (where ln $(k_{ls})_{calc}$ is obtained from applying eq 2 and ln $(k_{ls})_{exp}$ is determined experimentally) were used by Schenkluhn[7] and Brown[8] to quantitatively assess the utility of eq 2 in the modeling of a quantifiable reaction property.

Table II. $E_{1/2}$ Values for the Ruthenium(III/II) Couples and UV–Visible Spectroscopic Data for the $[Ru(Cl)(N\text{-}N)(trpy)]^{2+}$ and $[Ru(H_2O)(N\text{-}N)(trpy)]^{2+}$ Complexes

complex	$E_{1/2}$[a]	λ (nm) (ϵ (10^3 M^{-1} cm^{-1}))[b]
1[c,d]	0.93	236 (sh), 254 (sh), 283 (26.8), 295 (30.1), 318 (26.2), 359 (sh), 506 (9.0)
2[c,d]	0.93	267 (59.0), 278 (sh), 302 (sh), 377 (sh), 434 (sh), 504 (10.8)
3[c,d]	0.89	266 (65.3), 278 (sh), 302 (sh), 319 (30.6), 434 (sh), 508 (10.3)
4[c,d]	0.95	274 (48.0), 323 (28.0), 386 (5.8), 522 (9.5)
5[c,d]	0.97	271 (55.6), 337 (37.7), 340 (sh), 481 (sh), 589 (11.4)
6[c,d]	1.02	272 (24.8), 276 (sh), 315 (27.1), 362 (sh), 543 (8.3)
7[e]	0.75	275 (sh), 290 (35.8), 309 (34.9), 355 (sh), 475 (10.5)
8[e]	0.75	264 (63.4), 277 (sh), 282 (sh), 304 (30.8), 408 (sh), 472 (11.6)
9[e]	0.73	264 (60.3), 282 (sh), 312 (30.5), 406 (sh), 474 (10.9)
10[e]	0.81	271 (48.6), 278 (sh), 305 (29.7), 387 (sh), 488 (10.2)
11[e]	0.80	264 (40.2), 279 (sh), 319 (26.3), 335 (sh), 353 (sh), 373 (sh), 503 (sh), 550 (8.8)
12[e]	0.85	273 (20.8), 307 (39.3), 487 (7.5)

[a] $E_{1/2} = (E_{p,a} + E_{p,c})/2$, V vs SSCE. [b] sh = shoulder. [c] $E_{1/2}$ measured in 0.1 M tetrabutylammonium tetrafluoroborate (TBAB)/CH_2Cl_2. [d] UV–vis spectra recorded in CH_2Cl_2. [e] Measured in pH = 2.2 HNO_3/$NaNO_3$, μ = 0.1 M.

In order to extract the steric ligand effects from our ligand substitution rate constant data, we needed a quantitative measure of the electronic ligand effects. Allman and Goel estimated phosphine electronic ligand effects from the chemical shifts (δ) and coupling constants (J) of the protonated phosphines obtained in trifluoroacetic acid as well as the ^{13}C NMR chemical shifts of the unprotonated phosphines.[10] The electronic contributions to the reactivity of phosphine containing complexes were obtained through the use of Kabachnik's σ^{ϕ} values which were derived from the ionization of phosphorus acids.[11b] The electronic parameter, υ, derived from the A_1 carbonyl stretching frequency of $Ni(CO)_3PR_3$ complexes[12,13] has also commonly been used as a measure of the ligand electronic effects. Unfortunately, these parameters (δ, J, σ^{ϕ}, and υ) are specific to phosphine ligands and have no readily available equivalent when one considers bidentate bipyridyl ligands. Giering and co-workers have supported the use of pK_a values and half- neutralization potentials (HNP) as an easily attainable measure of the σ-donicity of the phosphine ligands.[3] As pK_a values of most of the protonated forms of the bidentate ligands were available,[31] they were used as the electronic parameter in eq 2.

Notably, we did not utilize the redox potentials for the ruthenium(III/II) couples as a possible measure of electronic ligand effects. For the $[Ru(H_2O)(N\text{-}N)(trpy)]^{2+}$ complexes, the $E_{1/2}$ values for the ruthenium(III/II) couples decrease in the order N-N = 6,6′-Cl_2bpy > 2,9-Me_2phen > biq > bpy = phen > 4,7-Me_2phen (Table II). This order of the potential values of these ruthenium(III/II) couples does not reflect the order based on the pK_a values of the protonated forms of the bipyridyl ligands (6,6′-Cl_2bpy > biq > bpy > phen > 4,7-Me_2phen > 2,9-Me_2phen), as demonstrated by a plot of the $E_{1/2}$ values of the $[Ru(H_2O)(N\text{-}N)(trpy)]^{2+}$ complexes versus the pK_a values of the protonated forms of the bidentate ligands which gave $R^2 = 0.50$ ($E_{1/2} = -1.39 \times 10^2$ (pK_a) + 0.838). Since ligands can sterically affect

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(38) Hanckel, J. M.; Lee, K.-W.; Rushman, P.; Brown, T. L. *Inorg. Chem.* **1986**, *25*, 1852–1856.

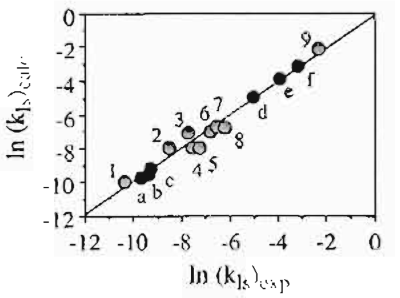

Figure 2. Correlation of the ln of the experimentally determined rate constant, ln $(k_{ls})_{exp}$, for the ligand substitution of the aqua ligand of $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ with CH_3CN vs the ln of the calculated rate constant for ligand substitution, ln $(k_{ls})_{calc}$. The best fit line for this correlation is described by the equation ln $(k_{ls})_{calc} = 0.947$ ln $(k_{ls})_{exp} - 0.369$ ($R^2 = 0.948$). The ln $(k_{ls})_{calc}$ values were obtained from the function ln $(k_{ls})_{calc} = 0.16(pK_a) + 0.15(\theta) - 29$. PR_3 ligands in the $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ complexes: 1 = PMe_3, 2 = PEt_3, 3 = $P(C_6H_4F)_3$, 4 = $P(n\text{-}Pr)_3$, 5 = $P(n\text{-}Bu)_3$, 6 = $P(C_6H_4CH_3)_3$, 7 = $P(C_6H_4OCH_3)_3$, 8 = $P(C_6H_5)_3$, 9 = PCy_3. Bidentate bipyridyl ligands in the $[Ru(H_2O)(N\text{-}N)(trpy)]^{2+}$ complexes: a = phen, b = bpy, c = 4,7-Me_2phen, d = biq, e = 6,6′-Cl_2bpy, f = 2,9-Me_2phen.

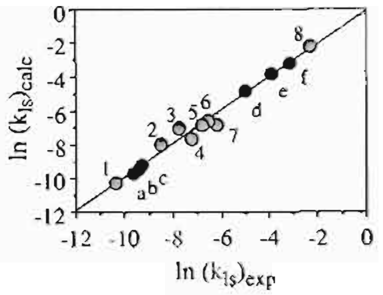

Figure 3. Correlation of the ln of the experimentally determined rate constant, ln $(k_{ls})_{exp}$, for the ligand substitution of the aqua ligand of $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ with CH_3CN vs the ln of the calculated rate constant for ligand substitution, ln $(k_{ls})_{calc}$. The best fit line for this correlation is described by the equation ln $(4k_{ls})_{calc} = 0.959$ ln $(k_{ls})_{exp} - 0.287$ ($R^2 = 0.959$). The ln $(k_{ls})_{calc}$ values were obtained from the function ln $(k_{ls})_{calc} = 0.058(pK_a) + 0.10(E_R) - 15$. PR_3 ligands in the $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ complexes: 1 = PMe_3, 2 = PEt_3, 3 = $P(C_6H_4F)_3$, 4 = $P(n\text{-}Bu)_3$, 5 = $P(C_6H_5)_3$, 6 = $P(C_6H_4OCH_3)_3$, 7 = $P(C_6H_4CH_3)_3$, 8 = PCy_3. Bidentate bipyridyl ligands in the $[Ru(H_2O)(N\text{-}N)(trpy)]^{2+}$ complexes: a = phen, b = bpy, c = 4,7-Me_2phen, d = biq, e = 6,6′-Cl_2bpy, f = 2,9-Me_2phen.

Table III. Second-Order Rate Constants for the Exchange of the Water Ligand with Acetonitrile for the Complexes $[Ru(H_2O)(N\text{-}N)(trpy)]^{2+}$, pK_a Values for the Protonated Forms of the Bidentate Ligands, Calculated Cone Angles, and Calculated E_R Values for the Bidentate Ligands

complex	10^4k (M^{-1} s^{-1})[a]	pK_a	θ (deg)[b]	E_R[c]
7	0.75	4.37[d]	126	49
8	0.62	4.88[d]	124	47
9	0.79	5.94[d]	125	49
10	410	6.15[d]	167	108
11	69	3.32[e]	158	93
12	200	−0.153[e]	169	105

[a] pH = 2.2 $HNO_3/NaNO_3$ ($\mu = 0.1$ M), at 25 °C. [b] Cone angles were calculated from the equation: ln $(k_{ls})_{calc} = 0.016(pK_a) + 0.15(\theta) - 29$. [c] E_R values were calculated from the equation ln $(k_{ls})_{calc} = 0.058(pK_a) + 0.10(E_R) - 15$. [d] pK_a values were taken from ref 31. [e] pK_a value was obtained by extrapolation of the half-neutralization potentials.

the redox potentials of metal couples, we concluded that redox potentials may not be appropriate measures of the electron density around a metal center for the $[Ru(H_2O)(N\text{-}N)(trpy)]^{2+}$ complexes.[3,39,40]

In our previous study,[29] we used Tolman's cone angles as a quantitative measure of the steric ligand effects of tertiary phosphine ligands. The cone angle (θ) is the apex angle of a cylindrical cone, 2.28 Å from the center of the P atom, which just touches the van der Waals radii of the outermost atoms of the CPK model.[13] A second method for quantifying steric ligand effects using E_R values was recently developed by Brown and co-workers, with the use of MM2 calculations.[8] Using linear regression techniques, we fit the general equation, eq 2, for the $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ complexes, and the graphs representing the correlations between the calculated and experimental ln k_{ls} values are given in Figures 2 and 3. Equation 3 ($R^2 = 0.948$)

$$\ln k_{ls} = 0.16(pK_a) + 0.15(\theta) - 29 \qquad (3)$$

was obtained when ln k_{ls} was used as the reactivity parameter, the pK_a of the phosphine ligand was used as the electronic parameter, and θ was used as the steric parameter (Figure 2). From this equation we can propose that ln k_{ls} has an 86% steric contribution and only a 14% electronic contribution. This steric contribution is quite large, especially when compared with the results of Kochi for ligand substitution on manganese complexes where the steric contribution to ln k_{ls} was 55% and the electronic contribution 45%.[5] When E_R values were used as the steric parameters and the pK_a values of the protonated phosphine ligands were used as the electronic parameters, eq 4 was obtained (see

$$\ln k_{ls} = 0.058(pK_a) + 0.10(E_R) - 15 \qquad (4)$$

Figure 3) ($R^2 = 0.959$). From this equation we can propose that ln k_{ls} has a 95% steric contribution and only a 5% electronic contribution. The sign of the electronic constant, *a*, for the above two equations shows that rate of the reaction is enhanced by electron-donating groups. Also, the sign of the steric constant, *b*, for the above two equations indicates that increasing the steric size of the phosphine ligand accelerates the rate of the reaction. These two observations are consistent with our previous assertion that, for the $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ complexes, ligand exchange involves a dissociative interchange mechanism.[29]

In order to assess the steric ligand properties of the six bidentate ligands of interest, the constants *a*–*c* that were found for the $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ complexes (eqs 3 and 4) were then used when eq 2 was applied to the $[Ru(H_2O)(N\text{-}N)(trpy)]^{2+}$ complexes. The calculated cone angles and E_R values for the six bidentate ligands are listed in Table III. The similarity of the cone angles and E_R values for bpy, phen, and 4,7-Me_2phen was expected due to the similar structure of these three ligands. Furthermore, these estimates indicate that bpy, phen and 4,7-Me_2phen exert steric effects similar to the PMe_3 (cone angle = 118° and E_R value = 39) and PEt_3 (cone angle = 132° and E_R value = 61) ligands. The biq ligand is significantly larger than bpy, phen, and 4,7-Me_2phen, and the cone angle of biq can be compared to that of the PPh_3 ligand (cone angle 145°), and the E_R value for biq is comparable to those for the $PEt_2(t\text{-}Bu)$ and $P(i\text{-}Pr)_2Et$ ligands at E_R = 90 and 91, respectively. The calculated cone angles values for 6,6′-Cl_2bpy and 2,9-Me_2phen are similar, and these two ligands are larger than the biq ligand. The cone angles of 6,6′-Cl_2bpy and 2,9-Me_2phen are comparable to those of the $P(i\text{-}Pr)_3$ and PCy_3 ligands (cone angles = 160 and 170°, respectively), and E_R values are comparable to those of $P(i\text{-}Pr)_3$ and $PPhCy_2$ (E_R = 109 and 105, respectively). Finally, the calculated cone angles for the bidentate bipyridyl ligands can also be compared with those of bischelating phosphine ligands. Tolman measured the cone angles of the following bidentate phosphine ligands (when the PMP angle was assumed to be 85°): $Et_2PCH_2CH_2PEt_2$ (depe), 115°; $Ph_2PCH_2CH_2PPh_2$ (dppe), 125°; $Cy_2PCH_2ch_2pcY_2$ (DCPE), 142°.[13] It should be noted that the bidentate bipyridyl ligands should display anisotropic steric effects, due to the planarity of the bipyridyl ligands, unlike the tertiary

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(39) Bohling, D. A.; Evans, J. F.; Mann, K. R. *Inorg. Chem.* **1982**, *21*, 3546–3551.

(40) Walker, D. D.; Taube, H. *Inorg. Chem.* **1981**, *20*, 2828–2834.

phosphine ligands, which display isotropic steric effects (with respect to the Ru–P axis). Thus, an important caution in the use of cone angles with bidentate ligands is that the steric effects of bidentate bipyridyl ligands should be more pronounced in the plane of the bidentate ligand. In order to test this hypothesis, we used CPK models to measure the in-plane cone angles of the bidentate bipyridyl ligands, using a technique similar to Tolman's original technique for evaluating cone angles. The measured in-plane cone angles of the bipyridyl ligands are as follows: bpy, 118°; phen, 118°; 4,7-Me_2phen, 118°; biq, 157°; 2,9-Me_2phen, 160°; 6,6′-Cl_2bpy, 167°. Since these values agree well with our values from ligand substitution, we suggest that, for ligand substitution involving the $[Ru(H_2O)(N\text{-}N)(trpy)]^{2+}$ complexes, the bipyridyl ligands (N-N) exert the majority of their steric ligand effects in the plane of the bidentate ligand.

In conclusion, through the use of eqs 2 and 3, ligand substitution rate constant data, and pK_a values, we developed a method of assessing the electronic and steric ligand effects of six bidentate bipyridyl ligands. We quantitatively described the size of the bidentate ligands (in terms of cone angles and E_R values) as bpy $\cong$ phen $\cong$ 4,7-Me_2phen < biq < 6,6′-Cl_2bpy $\cong$ 2,9-Me_2phen. Due to the recent assertions in the chemistry literature that the steric ligand effects may substantially affect the redox reactivity of transition metal complexes,[21,25,26] one possible application of the quantitative size estimates of the bidentate bipyridyl ligands presented here may be in the rational design of new redox reagents or catalysts.

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