Remarkable Spectator Ligand Effect on the Rate Constant of Ligand Substitution of (Aqua)ruthenium(II) Complexes

My Hang V. Huynh,*,†,‡ Joanne M. Lasker,† Modi Wetzler,† Brendan Mort,† Lisa F. Szczepura,*,§ Laura M. Witham,† Jose M. Cintron,† Amy C. Marschilok,† Lily J. Ackerman,§ Ronald K. Castellano,|| Donald L. Jameson,*,|| Melvyn Rowen Churchill,† Alan J. Jircitano,⊥ and Kenneth J. Takeuchi*,†

Contribution from the Chemistry Department, State University of New York at Buffalo, Buffalo, New York, 14260, the Chemistry Department, Gettysburg College, Gettysburg, Pennsylvania, 17325, the Chemistry Department, Illinois State University Normal, Illinois 61790, and the Chemistry Division, MS J514, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Received December 7, 2000

Abstract: The influence of two different di(1-pyrazolyl)alkane ligands on the rate constant of aqua ligand substitution of ruthenium(II) complexes with the formula $[Ru(H_2O)(L_2)(tpmm)]^{2+}$ (L_2 = di(1-pyrazolyl)methane (DPMet) or 2,2-di(1-pyrazolyl)propane (DPPro)) was investigated. A 9.4×10^5-fold increase in the rate constant of ligand substitution at pH = 6.86 was observed when DPMet was replaced with DPPro. This remarkable increase was unexpected, considering that these bidentate ligands appear quite similar. To help lend insight into this dramatic spectator ligand effect, the activation parameters for the ligand substitution reactions were determined, and single-crystal X-ray data were collected on the structurally analogous (chloro)ruthenium(II) complexes, $[Ru(Cl)(L_2)(tpmm)]^+$. These results are discussed in the context of a heteroscorpionate effect exerted by the DPPro ligand.

Introduction

In 1967, Trofimenko reported the preparation of the first poly(pyrazolyl)borate ligands.[1] He later referred to tridentate poly(pyrazolyl) ligands as scorpionate ligands, relating the facial coordination of these pyrazolyl ligands as analogous to a scorpion (the ligand) grabbing (bonding with two donor atoms) and then stinging (bonding with the third donor atom) its prey (the metal center).[2] Homoscorpionate ligands, such as (1-pyrazolyl)$_3$BH$^-$ and (1-pyrazolyl)$_3$CH, contain three identical pyrazolyl-based donor groups; a number of homoscorpionate ligands have been synthesized and coordinated to metal centers.[3] Heteroscorpionate ligands contain two identical pyrazolyl donor groups (the scorpion "pincers") and a different donor group (the scorpion "stinger") that can coordinate to a metal center. For example, ligands with the basic formula (1-pyrazolyl)$_2$CHX (where X is a functionalized donor such as a substituted phenol or thiol) were reported recently and display heteroscorpionate ligand property when coordinated with metals.[4,5]

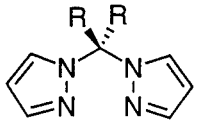

Figure 1. 2,2-Di(1-pyrazolyl)alkane ligands (DPMet, R = H; DPPro, R = Me).

Related in concept to the heteroscorpionate ligands is a family of di(1-pyrazolyl)alkane ligands, which bind to a metal center through two pyrazolyl groups (Figure 1). These flexible bidentate ligands have been shown to coordinate to metals that display a variety of coordination geometries.[6−8] While these ligands do not have a third donor group that can bond to the metal center, the third substituent on the carbon bridgehead may display significant interaction with either the metal center or other ligands bonded to the metal center, which we will refer to as a heteroscorpionate ligand effect. For example, consider the ligand DPPro, where DPPro = 2,2-di(1-pyrazolyl)propane. DPPro is a bidentate ligand that positions a third group (namely, a methyl group on the carbon bridgehead) in close proximity to the metal center. In the solid-state structure of the square planar $[Pd(Cl)_2$-(DPPro)] complex, there is an agostic interaction between the methyl hydrogen and the metal center.[9] Thus, the interaction

* Corresponding authors. (K.J.T.) Phone: 1-716-654-6800, ext 2136. Fax: 1-716-645-6963. E-mail: takeuchi@nsm.buffalo.edu. (M.H.V.H.) Phone: 1-505-667-3968. Fax: 1-505-667-3314. E-mail: huynh@lanl.gov. (L.F.S.) Phone: 1-309-438-2359. Fax: 1-309-438-5538. E-mail: lfszcze@ilstu.edu. (D.L.J.) Phone: 1-717-337-6257, Fax: 1-717-337-6251. E-mail: djameson@gettysburg.edu

† State University of New York at Buffalo.

‡ Los Alamos National Laboratory.

§ Illinois State University Normal.

|| Gettysburg College.

⊥ School of Science, Pennsylvania State University at Erie−Behrend College, Erie, PA 16563.

(1) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288−6294.

(2) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943−980 and references therein.

(3) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.

(4) Hammes, B. S.; Carrano, C. J. *Inorg. Chem.* **1999**, *38*, 3562−3568.

(5) Higgs, T. C.; Dean, N. S.; Carrano, C. J. *Inorg. Chem.* **1998**, *37*, 1473−1482.

(6) Pettinari, C.; Cingolani, A.; Bovio, B. *Polyhedron* **1996**, *15*, 115−126.

(7) Tang, L.; Wang, Z.; Xu, Y.; Wang, J.; Wang, H.; Yao, X. *Polyhedron* **1998**, *17*, 3765−3769.

(8) Hermann, W. A.; Roesky, P. W.; Kuhn, F. E.; Elison, M.; Artus, G.; Scherer, W.; Romao, C. C.; Loper, A.; Basset, J.-M. *Inorg. Chem.* **1995**, *34*, 4701−4707.

(9) Minghetti, G.; Cinellu, M. A.; Bandini, A. L.; Banditelli, G.; Demartin, F.; Manassero, M. *J. Organomet. Chem.* **1986**, *315*, 387−399.

10.1021/ja0041977 CCC: $20.00
Published on Web 08/16/2001

between the methyl group of the DPPro ligand and the Pd center is heteroscorpionate in nature.

In this study, two types of complexes were prepared, characterized, and studied, namely, $[Ru(Cl)(L_2)(tpmm)]^+$ and $[Ru(H_2O)(L_2)(tpmm)]^{2+}$ (where L_2 = di(1-pyrazolyl)methane (DPMet) or DPPro and tpmm = tri(2-pyridyl)methoxymethane). The $[Ru(Cl)(L_2)(tpmm)]^+$ complexes provided important X-ray crystal structure information, and the kinetics of ligand substitution for the $[Ru(H_2O)(L_2)(tpmm)]^{2+}$ complexes provided unusual differences in the rate constant values, depending on the identity of L_2. The results of this study establish that a heteroscorpionate ligand effect can be surprisingly large with regard to the modification of the rate of ligand substitution at a ruthenium(II) center.

The rate constant of ligand substitution for $[Ru(H_2O)(DPMet)(tpmm)]^{2+}$ is 7.0×10^{-5} M^{-1} s^{-1} at pH = 6.86, which is reminiscent of that for $[Ru(H_2O)(bpy)(trpy)]^{2+}$ (bpy = 2,2′-bipyridine, trpy = 2,2′:6′,2″-terpyridine, and rate constant of ligand substitution at pH = 2.2 is 7.5×10^{-5} M^{-1} s^{-1}).[10] On the basis of the electronic ligand effect, similar rate constants were expected because $[Ru(H_2O)(DPMet)(tpmm)]^{2+}$ possesses three pyridyl donors and two pyrazolyl donors, with a pyridyl donor trans to the aqua ligand, while $[Ru(H_2O)(bpy)(trpy)]^{2+}$ possesses five pyridyl donors with a pyridyl donor trans to the aqua ligand. Using similar logic, when the rate constant for the ligand substitution of $[Ru(H_2O)(DPPro)(tpmm)]^{2+}$ was measured, it would have been reasonable for the value to be close in magnitude to the rate constant for $[Ru(H_2O)(DPMet)(tpmm)]^{2+}$ since the electronic ligand effects for both complexes are very similar. However, when DPMet was replaced with DPPro, a striking 9.4×10^5-fold increase in the rate constant of ligand substitution at pH = 6.86 was observed! This enhancement was unexpected, considering that the only structural difference between DPMet and DPPro is that DPMet has H substituents on the carbon bridgehead, whereas DPPro has CH_3 substituents on the carbon bridgehead. The unusual increase in the rate constant, resulting from this H to CH_3 substituent change on the spectator ligand, can be rationalized by a possible heteroscorpionate effect by DPPro on the aqua leaving group.

Experimental Section

Materials. Tpmm was prepared according to literature procedures.[11] DPMet and DPPro were also prepared according to literature procedures.[12] The synthesis and characterization of $[Ru(CH_3CN)(DPMet)(tpmm)](PF_6)_2$ and $[Ru(CH_3CN)(DPPro)(tpmm)](BF_4)_2$ are reported in the Supporting Information.

Preparation of $[Ru(Cl)_3(tpmm)]$. A 1.00-g (3.82 mmol) sample of $[RuCl_3 \cdot 3H_2O]$ and 892 mg (3.82 mmol) of tpmm were added to 100 mL of absolute ethanol under N_2, and the resultant mixture was heated at reflux for 8 h. The precipitated green solid was collected by vacuum filtration and washed with cold ethanol. Yield: 1.845 g (95.5%). Anal. Calcd for $RuC_{17}H_{15}N_3OCl_3 \cdot 0.5CH_3CH_2OH$: C, 42.58; H, 3.57; N, 8.28. Found: C, 42.64; H, 3.46; N, 8.15.

Preparation of [Ru(Cl)(DPMet)(tpmm)](X) (X = BF_4^- or PF_6^-) (1·X). A 400-mg (0.825 mmol) sample of $[Ru(Cl)_3(tpmm)]$, 135 mg (0.908 mmol) of DPMet, and 1.0 mL of $N(C_2H_5)_3$ were added to 80 mL of an 80:20 (v/v) ethanol:water mixture containing LiCl (0.908 mmol). The mixture was heated at reflux for 8 h under N_2. The resulting solution was filtered through diatomaceous earth and washed with ethanol. The volume of the filtrate was reduced, and an excess of $NaBF_4$ or NH_4PF_6 was added to precipitate the desired salt. The resulting solid was collected by vacuum filtration and washed with cold aqueous saturated $NaBF_4$ or NH_4PF_6 solution. The crude solid was purified by column chromatography on silica gel using methanol in CH_2Cl_2 (~0.5:100 v/v) as the eluent. The second band was collected, and its volume was reduced to yield a yellow solid. The solid was isolated by vacuum filtration. [Ru(Cl)(DPMet)(tpmm)](BF_4). yield: 0.491 g (94.2%). UV−visible data (CH_2Cl_2) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 372 (1.4×10^4); 282 sh (7.2×10^3); 250 (1.9×10^4). Anal. Calcd for $RuC_{24}H_{23}N_7OClBF_4 \cdot H_2O$: C, 43.22; H, 3.78. Found: C, 43.38; H, 4.15. ^1H NMR ($CDCl_3$): δ 4.10 (s, 3H), 6.25 (d, 1H), 6.37 (s, 2H), 6.50 (s, 2H), 6.80 (t, 1H), 7.16 (d, 1H), 7.25 (t, 2H), 7.75 (t, 1H), 7.9−8.0 (m, 6H), 8.48 (s, 2H), 9.10 (d, 2H).

Preparation of [Ru(Cl)(DPPro)(tpmm)](BF_4) (2·BF_4). A 400-mg (0.825 mmol) sample of $[Ru(Cl)_3(tpmm)]$, 160 mg (0.908 mmol) of DPPro, and 1.0 mL of $N(C_2H_5)_3$ were added to 80 mL of 80:20 (v/v) ethanol:water mixture containing LiCl (8.25 mmol). The solution was heated at reflux for 12 h under N_2. The solution was then filtered to remove insoluble materials before its volume was reduced, and an excess of $NaBF_4$ was added to precipitate the tetrafluoroborate salt. The resulting solid was collected by vacuum filtration and washed with cold aqueous saturated $NaBF_4$ solution. The crude solid was then purified by gradient column chromatography on silica gel, using 0.0−1.2% of methanol in CH_2Cl_2 as the eluent. The seventh band was collected, and the volume was reduced to precipitate an orange solid that was isolated using vacuum filtration. Yield: 0.236 g (42.0%). UV−visible (CH_2Cl_2) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 415 sh (8.3×10^3); 372 (1.1×10^4); 283 sh (5.0×10^3); 254 (1.3×10^4). ^1H NMR (CD_2Cl_2): δ 2.83 (s, 3H), 2.89 (s, 3H), 4.06 (s, 3H), 5.81 (d, 1H), 6.41 (s, 2H), 6.69 (s, 2H), 6.79 (t, 1H), 7.42 (m, 2H), 7.62 (t, 1H), 7.94−7.95 (m, 5H), 8.25 (d, 2H), 9.38 (d, 2H). Anal. Calcd for $RuC_{26}H_{27}N_7OClBF_4 \cdot 0.3CH_2Cl_2$: C, 44.98; H, 3.96; N, 13.96. Found: C, 45.02; H, 4.08; N, 14.11.

Preparation of $[Ru(H_2O)(DPMet)(tpmm)](PF_6)_2$ (3·$(PF_6)_2$). A 300-mg (0.450 mmol) sample of [Ru(Cl)(DPMet)(tpmm)](PF_6) was dissolved in 60 mL of a 30:70 (v/v) acetone:water mixture. A 2-mL aqueous solution of $AgBF_4$ (0.554 mmol) was added, and the mixture was heated at reflux for 1 h under N_2. After allowing the mixture to cool, the solution was filtered to remove the AgCl precipitate. A solution containing 5 equiv (2.31 mmol) of NH_4PF_6 was added to the filtrate, and the volume was reduced to precipitate the yellow solid. The solid was isolated using vacuum filtration and washed with cold water. Yield: 0.331 g (93.0%). $E_{1/2}$ = 0.436 V versus SSCE in pH = 6.86 KH_2PO_4/Na_2HPO_4 aqueous solution (μ = 0.1 M). UV−visible data (pH = 2.00 $HNO_3/NaNO_3$ aqueous solution) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 367 (1.0×10^4); 304 (1.0×10^4); 271 (9.5×10^3). ^1H NMR (D_2O): δ 4.00 (s, 3H), 6.27 (d, 1H), 6.40 (s, 2H), 6.49 (d, 1H), 6.67 (t, 1H), 6.86 (s, 2H), 6.93 (d, 1H), 7.32 (t, 2H), 7.62 (t, 1H), 7.84−7.94 (m, 3H), 8.09 (d, 2H), 8.19 (s, 2H), 8.54 (d, 2H). Anal. Calcd for $RuC_{24}H_{25}N_7O_2P_2F_{12} \cdot 0.05\ Bu_4NPF_6$: C, 34.44; H, 3.36; N, 11.33. Found: C, 34.17; H, 3.44; N, 10.95.

Preparation of $[Ru(H_2O)(DPPro)(tpmm)](BF_4)_2$ (4·$(BF_4)_2$). A 200-mg (0.278 mmol) sample of [Ru(Cl)(DPPro)(tpmm)](BF_4) was placed in 20 mL of water and the resultant mixture stirred for 2 h without heating. A $NaBF_4$ solution (8.19 mmol) was then added, and the volume of the resulting solution was reduced to precipitate the yellow solid. The solid was isolated using vacuum filtration. Yield: 0.208 g (79.0%). $E_{1/2}$ = 0.395 V versus SSCE in pH = 6.86 KH_2PO_4/Na_2HPO_4 aqueous solution (μ = 0.1 M). UV−visible data (pH = 2.00 $HNO_3/NaNO_3$ aqueous solution) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 362 (8.3×10^3); 304 (1.1×10^4); 271 (9.5×10^3). ^1H NMR (D_2O): δ 2.17 (s, 3H), 2.67 (s, 3H), 3.87 (s, 3H), 5.64 (d, 1H), 6.26 (s, 2H), 6.47 (m, 1H), 6.83 (d, 2H), 7.32 (m, 2H), 7.44 (m, 1H), 7.69 (d, 1H), 7.86 (m, 2H), 8.01 (d, 2H), 8.25 (d, 2H), 8.69 (d, 2H). Anal. Calcd for $RuC_{26}H_{29}N_7O_2B_2F_8 \cdot 1.5\ NaBF_4 \cdot 2\ H_2O$: C, 32.97; H, 3.51. Found: C, 32.77; H, 3.48.

At a later stage of this work, we discovered a more convenient and direct method for the preparation of $\mathbf{4}^{2+}$. After refluxing the reaction mixture of $\mathbf{2}^+$ for 12 h, the solution was cooled to room temperature. The reflux apparatus was replaced by a distillation apparatus. EtOH and NEt_3 were removed by distillation under N_2. The yellow aqueous

(10) Bessel, C. A.; Margarucci, J. A.; Acquaye, J. H.; Rubino, R. S.; Crandall, J.; Jircitano, A. J.; Takeuchi, K. J. *Inorg. Chem.* **1993**, *32*, 5779−5784.

(11) Wibaut, J. P.; de Jonge, A. P.; Van der Voort, H. G. P.; Otto, H. L. *Recl. Trav. Chim. Pays-Bas* **1951**, *70*, 1054−1056.

(12) Jameson, D. L.; Castellano, R. K.; Reger, D. L.; Collins, J. E.; Tolman, W. B.; Tokar, C. J. *Inorg. Syn.* **1998**, *32*, 51−63.

Table 1. Crystallographic Data for [Ru(Cl)(DPMet)(tpmm)](BF_4) (**1**·(BF_4)) and [Ru(Cl)(DPPro)(tpmm)](BF_4)·CH_2Cl_2 (**2**·(BF_4)·CH_2Cl_2)

	1·(BF_4)	**2**·(BF_4)·CH_2Cl_2
molecular formula	$C_{24}H_{23}BClF_4N_7ORu$	$C_{27}H_{29}BCl_3F_4N_7ORu$
fw	648.8	761.8
crystal system	orthorhombic	monoclinic
space group	$Pna2_1$ (C^9_{2v}; No. 33)	$P2_{1/c}$ (C^5_{2h}; No. 14)
a, Å	14.2466(10)	8.2913(13)
b, Å	14.9989(10)	13.6666(20)
c, Å	12.0496(8)	27.6335(41)
β, deg		91.354(13)
V, A^3	2574.8(3)	3130.4(8)
Z	4	4
color	orange columnar	orange plate
D (calcd), g cm^{-3}	1.674	1.616
wavelength, λ	0.710 73	0.710 73
temperature, K	293(2)	298
2θ range	3.9−56.6	6.0−45.0
index ranges	−18 _ h _ 18	0 _ h _ 8
	−19 _ k _ 14	0 _ k _ 14
	−15 _ *l* _ 13	−29 _ *l* _ 29
absorptn coeff, mm^{-1}	0.775	0.806
reflctns collected	16 228	4588
independent reflctns	5859	4073
reflctns observed	4515 (> $2\sigma_I$)	3158 (> $6\sigma_F$)
R indices (all data)	$R = 0.0672$	$R = 0.0636$
	w$R = 0.1294$ (F^2 refinement)	w$R = 0.0768$
R indices	$R = 0.0458$ ($2\sigma_I$ data or above)	$R = 0.0497$ ($6\sigma_F$ data)
	w$R = 0.1203$	w$R = 0.0574$
largest diff peak and hole, e^-/A^{-3}	+1.854 and −0.531	+1.30 and −0.81
goodness of fit	1.014	1.37

layer was loaded on a Sephadex column, and the yellow $Ru^{II}-OH_2^{2+}$ product was eluted with 0.1 M NH_4PF_6. Yields by this method usually exceeded 90%. Compared to the previous method, the yield was more than double, and the workup time decreased to $^1/_{15}$. The $Ru^{II}-Cl^+$ complex can be obtained directly from the $Ru^{II}-OH_2^{2+}$ complex by stirring it in CH_2Cl_2 containing 2 equiv of LiCl.

Kinetic Measurements. For the (aqua)ruthenium(II) complexes, the ligand exchange of the aqua ligand by the acetonitrile ligand was conducted in aqueous solution at 25 °C under pseudo-first-order conditions (100−9000-fold excess of acetonitrile). The pseudo-first-order rate constants were measured for six solutions of varying acetonitrile concentration. Next, these rate constants were plotted against CH_3CN concentrations to obtain the second-order rate constants. The fast rate constant for the aqua ligand substitution of $\mathbf{4}^{2+}$ necessitated the use of stopped flow techniques and fast spectroscopic detection. Thus, an Olis rapid scanning monochromator (Olis RSM-1000) equipped with a USA stopped flow was used to monitor the ligand substitution reaction for $\mathbf{4}^{2+}$. The slower rate constant for the aqua ligand substitution of $\mathbf{3}^{2+}$ allowed the use of a Genesys 5 spectrophotometer in conjunction with conventional mixing techniques to monitor the ligand substitution reaction.

Results

Crystal Structure of 1·(BF_4). Details of the data collection are provided in Table 1. Labeling of atoms in the [Ru(Cl)(DPMet)(tpmm)]$^+$ cation is illustrated in Figure 2, and selected interatomic bond lengths and angles are listed in Table 2. Ru−N(pyridyl) and Ru−N(pyrazole) bond distances typically lie between 2.00 and 2.20 Å,[13,14,15c] and all of the Ru−N bond distances reported here fall within that range. In this complex, the DPMet ligand is coordinated to the Ru center through two equivalent bonds, Ru(1)−N(5) = 2.087(5) Å and Ru(1)−N(7) = 2.096(5) Å. However, the Ru−N bond lengths of the tpmm ligand are not equivalent. Two of the ruthenium−pyridyl bonds are equivalent (Ru(1)−N(1) = 2.017(5) Å and Ru(1)−N(2) = 2.024(5) Å) and are shorter than the third linkage (Ru(1)−N(3) = 2.049(5) Å). The longest bond is trans to a pyrazolyl group. The Ru(1)−Cl(1) distance is 2.443(2) Å.

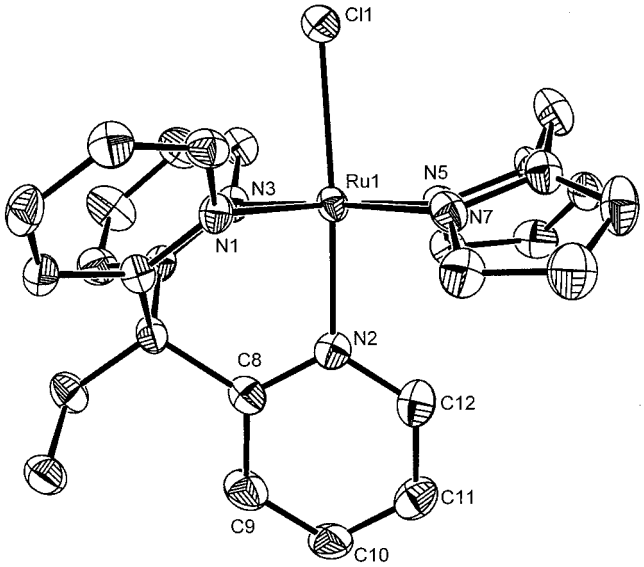

Figure 2. ORTEP diagram of [Ru(Cl)(DPMet)(tpmm)]$^+$ (50% probability). Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Ru(Cl)(DPMet)(tpmm)](BF_4) (**1**·(BF_4))

Ru(1)−Cl(1)	2.443(2)	Ru(1)−N(1)	2.017(5)
Ru(1)−N(2)	2.024(5)	Ru(1)−N(3)	2.049(5)
Ru(1)−N(5)	2.087(5)	Ru(1)−N(7)	2.096(5)
N(1)−Ru(1)−N(2)	88.13(19)	N(3)−Ru(1)−N(7)	176.97(19)
N(1)−Ru(1)−N(3)	87.32(18)	N(5)−Ru(1)−N(7)	86.96(18)
N(2)−Ru(1)−N(3)	88.4(2)	N(1)−Ru(1)−Cl(1)	89.53(14)
N(1)−Ru(1)−N(5)	176.83(18)	N(2)−Ru(1)−Cl(1)	176.29(15)
N(2)−Ru(1)−N(5)	88.85(18)	N(3)−Ru(1)−Cl(1)	88.64(14)
N(3)−Ru(1)−N(5)	91.62(18)	N(5)−Ru(1)−Cl(1)	93.43(13)
N(1)−Ru(1)−N(7)	93.95(18)	N(7)−Ru(1)−Cl(1)	94.11(14)
N(2)−Ru(1)−N(7)	88.93(19)		

Table 3. Selected Bond Distances (Å) and Angles (deg) for [Ru(Cl)(DPPro)(tpmm)](BF_4)·CH_2Cl_2 (**2**·(BF_4)·CH_2Cl_2)

Ru(1)−Cl(1)	2.463(2)	Ru(1)−N(31)	2.044(5)
Ru(1)−N(11)	2.095(5)	Ru(1)−N(41)	2.010(4)
Ru(1)−N(21)	2.090(5)	Ru(1)−N(51)	2.054(5)
Cl(1)−Ru(1)−N(11)	98.7(1)	N(11)−Ru(1)−N(51)	173.8(2)
Cl(1)−Ru(1)−N(21	96.3(1)	N(21)−Ru(1)−N(31)	175.8(2)
Cl(1)−Ru(1)−N(31)	87.8(1)	N(21)−Ru(1)−N(41)	87.2(2)
Cl(1)−Ru(1)−N(41)	174.0(1)	N(21)−Ru(1)−N(51)	93.6(2)
Cl(1)−Ru(1)−N(51)	87.5(1)	N(31)−Ru(1)−N(41)	88.7(2)
N(11)−Ru(1)−N(21)	86.7(2)	N(31)−Ru(1)−N(51)	85.5(2)
N(11)−Ru(1)−N(31)	93.8(2)	N(41)−Ru(1)−N(51)	87.4(2)
N(11)−Ru(1)−N(41)	86.4(2)		

Crystal Structure of 2·(BF_4)·CH_2Cl_2. Details of the data collection are provided in Table 1. Selected interatomic distances and angles are collected in Table 3. Labeling of atoms in the [Ru(Cl)(DPPro)(tpmm)]$^+$ cation is illustrated in Figure 3. The six-coordinate d^6 Ru(II) ion has a distorted octahedral environment. The Ru(1)−Cl(1) distance of 2.463(2) Å is typical for Ru(II)−Cl bond lengths.[14,15] Notably, the Ru(1)−Cl(1) distance is substantially longer than that found in $\mathbf{1}^+$. The DPPro ligand

(13) (a) Kojima, T.; Amano, T.; Ishii, Y.; Ohba, M.; Okaue, Y.; Matsuda, Y. *Inorg. Chem.* **1998**, *37*, 4076−4085. (b) Bhambri, S.; Tocher, D. A. *Polyhedron*, **1996**, *15*, 2763−2770. (c) Jimenez-Tenorio, M. A.; Jimenez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Inorg. Chim. Acta* **2000**, *300*−*302*, 869−874.

(14) Bruno, G.; Nicolo, F.; Schiavo, S. L.; Sinicropi, M. S.; Tresoldi, G. *J. Chem. Soc., Dalton Trans.* **1995**, 17−24.

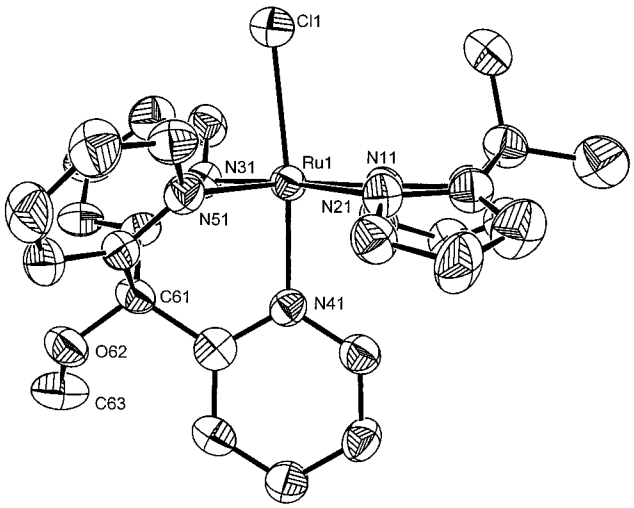

Figure 3. ORTEP diagram of $[Ru(Cl)(DPPro)(tpmm)]^+$ (50% probability). Hydrogen atoms are omitted for clarity.

Table 4. Rate Constants of Ligand Substitution (at 25 °C) and Activation Parameters for $[Ru(H_2O)(L_2)(tpmm)]^{2+}$ (pH = 6.86 KH_2PO_4/Na_2HPO_4 Aqueous Solution)

L_2	k_2 (M^{-1} s^{-1})	$\Delta H^{\ddagger}$ (kJ/mol)	$\Delta S^{\ddagger}$ (J/mol·K)
DPMet	7.0×10^{-5}	85 ± 2	-38 ± 5
DPPro	66	68 ± 2	17 ± 7

is linked to the ruthenium by two equivalent bonds (each of which is trans to a pyridyl fragment of the tpmm ligand) with Ru(1)−N(11) = 2.095(5) Å, Ru(1)−N(21) = 2.090(5) Å, and N(11)−Ru(1)−N(21) = 86.7°. In contrast to this, the tpmm ligand is linked to ruthenium with inequivalent Ru−N bonds. Thus, the bond trans to the chloride ligand (Ru(1)−N(41) = 2.010(4) Å) is significantly shorter than the remaining two Ru−tpmm linkages (Ru(1)−N(31) = 2.044(5) Å and Ru(1)−N(51) = 2.054(5) Å). The associated angles are N(31)−Ru(1)−N(41) = 88.7(2)°, N(31)−Ru(1)−N(51) = 85.5(2)°, and N(41)−Ru(1)−N(51) = 87.4(2)°.

Kinetic Studies. The rate constants for the substitution of the aqua ligand of **3**·$(PF_6)_2$ and **4**·$(BF_4)_2$ with acetonitrile were measured in an aqueous phosphate solution (pH = 6.86, μ = 0.1 M) at 25 °C. Both aqua complexes were found to be stable in phosphate solution for the duration of the kinetic experiments. The electronic spectra of both complexes were monitored, and all substitution reactions show isosbestic behavior (see Supporting Information), where the beginning and final spectra match the reactant and product, respectively. The ligand substitution of $\mathbf{3}^{2+}$ and $\mathbf{4}^{2+}$ displayed well-behaved second-order kinetics, and the specific rate constants are listed in Table 4. The precision of the measurements for all rate constants was 10% at a 95% confidence limit. The activation parameters were determined by measuring the rate constant of substitution at different temperatures (ranging from 20 to 50 °C) in aqueous phosphate solution (pH = 6.86) and plotting ln(k/T) versus $1/T$. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for both complexes are also presented in Table 4.

Discussion

Two new types of ruthenium(II) complexes, $[Ru(Cl)(L_2)(tpmm)]^+$ and the analogous $[Ru(H_2O)(L_2)(tpmm)]^{2+}$ (L_2 = DPMet or DPPro), were synthesized and characterized, including single-crystal X-ray structural analyses for both $[Ru(Cl)(L_2)(tpmm)]^+$ complexes. Note that only the alkane backbone of the bidentate L_2 ligands is varied, and the only difference between the L_2 ligands is that the third and fourth substituents on the carbon bridgehead in DPMet are Hs, while in DPPro they are Me groups (see Figure 1). We prepared these complexes in order to investigate a possible heteroscorpionate ligand effect that DPMet or DPPro might exert on the ligand substitution at the ruthenium(II) centers. The results were unexpected and striking, especially the magnitude of the ligand effect on the rate constant of the aqua ligand substitution (a 9.4×10^5-fold increase at pH = 6.86). This increase is, to the best of our knowledge, the largest ever reported for spectator ligand effect on the rate constant of ligand substitution at a ruthenium(II) center. As an example of ligand effect on rate constants of ligand substitution, in an earlier study involving $[Ru(H_2O)(L'_2)(trpy)]^{2+}$ complexes, we discovered that the rate constant of the aqua ligand substitution for the complex containing L'_2 = 2,9-dimethyl-1,10-phenanthroline (2,9-Me_2phen) was 660 times larger than that for the complex containing L'_2 = 1,10-phenanthroline (phen).[10] Notably, in both of the changes, from L'_2 = phen to L'_2 = 2,9-Me_2phen and from L_2 = DPMet to L_2 = DPPro, 2Hs were replaced with two Me groups; however, the observed increase in rate constant in the latter case is significantly greater.

We previously investigated the ligand substitution chemistry of (aqua)ruthenium(II) octahedral complexes, and we found that the mechanism of ligand substitution was dissociative interchange (I_d),[16] consistent with previous ruthenium(II) studies, such as those by Taube and Creutz.[17,18] Because of this mechanism, the magnitude of the rate constant for substitution of the aqua ligand for (aqua)ruthenium(II) complexes can be increased if the breaking of the aqua−ruthenium(II) bond is somehow made energetically easier. Thus, our earlier observations of sterically crowded ligands increasing the rate constant of the aqua ligand substitution by the acetonitrile ligand for (aqua)ruthenium(II) complexes were rationalized by steric and electronic effects, where a weakened aqua−ruthenium(II) bond resulted in an increase in the rate constant of the aqua ligand substitution.[10,16] Considering the unusually large increase in the rate constant of the aqua ligand substitution due to a substitution of Me groups for H substituents in the spectator ligand (i.e., DPPro versus DPMet), we examined the structural and kinetic differences between the two complexes closely.

To consider the enthalpic and entropic factors influencing the rate of ligand substitution, we measured the activation parameters for the substitution of the aqua ligand of $\mathbf{3}^{2+}$ and $\mathbf{4}^{2+}$ by the acetonitrile ligand (see Table 4). DPPro and DPMet are structurally very similar, with the primary difference being that DPPro positions one of the methyl groups in close proximity to the aqua ligand while DPMet positions one of the hydrogen substituents hydrogen in close proximity to the aqua ligand. The values obtained for the entropy and enthalpy of activation for these two complexes are consistent with a dissociative inter-

(15) (a) Shen, J.; Haar, C. M.; Stevens, E. D.; Nolan, S. P. *J. Organomet. Chem.* **1998**, 571, 205−213. (b) Jones, N. D.; MacFarlane, K. S.; Smith, M. B.; Schutte, R. P.; Rettig, S. J.; James, B. R. *Inorg. Chem.* **1999**, *38*, 3956−3966. (c) Szczepura, L. F.; Maricich, S. M.; See, R. F.; Churchill, M. R.; Takeuchi, K. J. *Inorg. Chem.* **1995**, *34*, 4198−4205.

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

(17) (a) Shepherd, R. E.; Taube, H. *Inorg. Chem.* **1973**, *12*, 1392−1401. (b) Isied, S. S.; Taube, H. *Inorg. Chem.* **1976**, *15*, 3070−3075. (c) Matsubara, T.; Creutz, C. *Inorg. Chem.* **1979**, *18*, 1956−1966.

(18) Allen, L. R.; Craft, P. R.; Durham, B.; Walsh, J. *Inorg. Chem.* **1987**, *26*, 53−56.

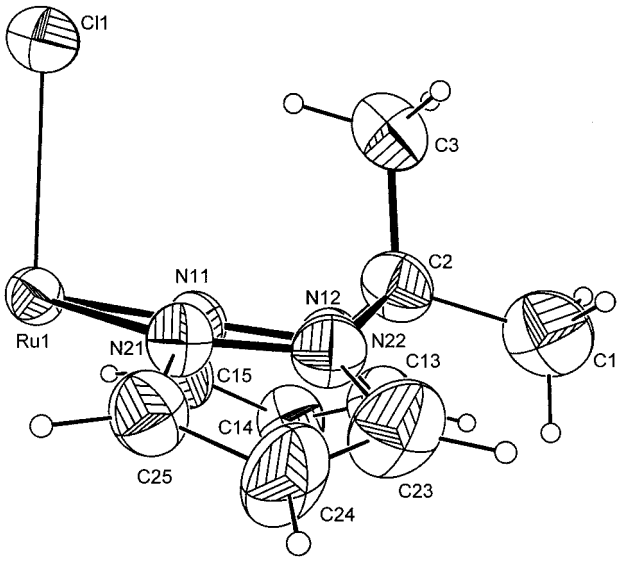

Figure 4. Partial ORTEP diagram of $[Ru(Cl)(DPPro)(tpmm)]^+$ with focus on the steric interaction between the chloride ligand and one of the methyl groups on the carbon bridgehead of the DPPro ligand.

change mechanism[17a,18,19] although there are considerable differences in values between the two complexes. $\Delta H^{\ddagger}$ for $\mathbf{4}^{2+}$ is substantially smaller (by 17 kJ/mol), indicating that it requires less energy to break the $Ru-OH_2$ bond in this complex compared to that in $\mathbf{3}^{2+}$. Thus, ligand exchange is enthalpically favored for $\mathbf{4}^{2+}$ relative to $\mathbf{3}^{2+}$. Further, $\Delta S^{\ddagger}$ for $\mathbf{4}^{2+}$ is much more positive than $\Delta S^{\ddagger}$ for $\mathbf{3}^{2+}$, indicating that ligand substitution is entropically favored for $\mathbf{4}^{2+}$ relative to $\mathbf{3}^{2+}$.

To determine structural differences that DPPro and DPMet might exert on the leaving group, single-crystal X-ray structures for the analogous complexes $[Ru(Cl)(DPMet)(tpmm)]^+$ and $[Ru(Cl)(DPPro)(tpmm)]^+$ were collected. We were unable to obtain crystals of the (aqua)ruthenium(II) complexes containing DPMet or DPPro suitable for X-ray analysis. Since Cl and H_2O occupy the same relative position in $[Ru(X)(L_2)(tpmm)]^{n+}$ (where X = Cl and $n = 1$ or X = H_2O and $n = 2$), we propose that structural interaction between L_2 and Cl may have relevance to possible interaction between L_2 and H_2O. Notably, there is a difference in the Ru−Cl bond lengths of the DPPro and DPMet complexes: Ru(1)−Cl(1) = 2.443(2) Å for $\mathbf{1}^+$ while Ru(1)−Cl(1) = 2.463(2) Å for $\mathbf{2}^+$. This difference of 0.02 Å suggests a possible weakening of the Ru−Cl bond in the DPPro complex relative to that in the DPMet complex. Furthermore, the $N(L_2)$−Ru−Cl angles (98.7(1)° and 96.3(1)°) of $\mathbf{2}^+$ are larger than the angles (93.43(13)° and 94.11(14)°) of $\mathbf{1}^+$.

Given the structural differences between $\mathbf{2}^+$ and $\mathbf{1}^+$, we propose that steric differences between DPPro and DPMet are largely responsible for the differences observed in the activation parameters and the rate constants of ligand substitution of the corresponding (aqua)ruthenium(II) complexes. Figure 4 shows the close interaction between one of the methyl groups of the DPPro ligand and the chloride ligand. If the steric interaction observed in the $[Ru(Cl)(L_2)(tpmm)]^+$ complexes is present in the analogous aqua complexes, we can interpret the differences in the activation parameters of the aqua ligand substitution studies based on these structural differences of the (chloro)ruthenium(II) complexes. For example, on the basis of the observed lengthening (or weakening) of the Ru−Cl bond in $\mathbf{2}^+$ relative to that in $\mathbf{1}^+$, we expect $\mathbf{4}^{2+}$ to have a weaker $Ru-OH_2$ bond than that of $\mathbf{3}^{2+}$. A weaker $Ru-OH_2$ bond should result in $\Delta H^{\ddagger}$ for $\mathbf{4}^{2+}$ being less positive than the $\Delta H^{\ddagger}$ for $\mathbf{3}^{2+}$, which is consistent with our $\Delta H^{\ddagger}$ measurements. Regarding the entropies of activation for I_d ligand substitution mechanisms, an increase in the degrees of freedom between the ground state and the transition state should lead to a more positive value of $\Delta S^{\ddagger}$. The $\mathbf{2}^+$ complex shows evidence of increased steric interaction between one of the substituents on the backbone of the bidentate ligand (methyl substituent) and the chloro ligand (vide supra). Therefore, we expect the freedom of rotation about the $Ru-OH_2$ bond in $\mathbf{4}^{2+}$ to be hindered due to the interaction of the aqua ligand with the methyl substituent of the DPPro ligand. This would cause the $\Delta S^{\ddagger}$ value for $\mathbf{4}^{2+}$ to be more positive than the $\Delta S^{\ddagger}$ value for $\mathbf{3}^{2+}$, which is in agreement with our observations.

Conclusion

In this paper, we have shown that the heteroscorpionate ligand effect of the bidentate di(1-pyrazolyl)alkane ligand, DPPro relative to DPMet, can influence the rates of ligand substitution at an octahedral transition metal center in an unprecedented manner. The observed increase of 9.4×10^5 for the rate constant of ligand substitution for $\mathbf{4}^{2+}$ relative to the rate constant of ligand substitution for $\mathbf{3}^{2+}$ is strikingly unexpected with only a H-to-Me spectator ligand substituent change and is primarily due to steric interaction.

Acknowledgment. K.J.T. acknowledges the National Science Foundation and Arco Chemical for partial financial support. M.H.V. Huynh gratefully acknowledges postdoctoral fellowship support from the Director's Office of Los Alamos National Laboratory. Los Alamos National Laboratory is operated by the University of California for the U.S. Department of Energy under Contract W-7405-ENG-36. M.R.C. acknowledges that the purchase of the diffractometer (SUNY at Buffalo) was made possible by Grant 89-13733 from the Chemical Instrumentation Program of the National Science Foundation. L.F.S. acknowledges Illinois State University for the start-up funds which allowed the purchase of the Olis RSM-1000 as well as Dr. S. R. Wilson (University of Illinois at Urbana−Champaign) for the collection of the X-ray data for the $[Ru(Cl)(DPMet)(tpmm)](BF_4)$ complex. This work is dedicated to Dr. Thomas J. Meyer (Associate Laboratory Director for Strategic and Supporting Research, Los Alamos National Laboratory, Los Alamos, NM 87545) on the occasion of his 60th birthday.

Supporting Information Available: Details of crystal structure determinations for compounds $\mathbf{1}\cdot(BF_4)$ and $\mathbf{2}\cdot(BF_4)\cdot CH_2Cl_2$, spectral data showing isosbestic behavior for the reaction of $[Ru(H_2O)(L_2)(tpmm)]^{2+}$ with acetonitrile, and synthesis and characterization of $[Ru(CH_3CN)(DPMet)(tpmm)](PF_6)_2$ and $[Ru(CH_3CN)(DPPro)(tpmm)](BF_4)_2$**.** This material is available free of charge via the Internet at http://pubs.acs.org. See any current masthead page for ordering information and Web access instructions.

JA0041977

(19) (a) Minniti, D. *Inorg. Chem.* **1994**, *33*, 2631−2634. (b) Pavlovic, D.; Sutic, D.; Asperger, S. *J. Chem. Soc., Dalton Trans.* 1976, 2406−2408.