Trans–Cis Isomerization in $[Os(tpy)(Cl)_2(N)]^+$

Darryl S. Williams,[1] George M. Coia, and Thomas J. Meyer*

Department of Chemistry, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599

Received March 18, 1994[⊗]

trans-$[Os(tpy)(Cl)_2(N)]Cl$ (**1**) has been prepared by addition of tpy to $[NBu_4][Os(N)Cl_4]$ in dichloromethane and *trans*-$[Os(tpy)(Cl)_2(N)][PF_6]$ (**2**) by addition of $[NH_4][PF_6]$ to a methanolic solution of **1**. When dissolved in methanol in the presence of added chloride, **1** undergoes slow isomerization to *cis*-$[Os(tpy)(Cl)_2(N)]^+$, which has been isolated as its $[PF_6]^-$ salt **3**. In methanolic solutions containing added chloride, an equilibrium is set up between the *trans* and *cis* isomers, *trans*-$[(tpy)(Cl)_2Os{\equiv}N]^+ \rightleftharpoons$ *cis*-$[(tpy)(Cl)_2Os{\equiv}N]^+$ with $K(20\ °C) = k_f/k_r = 4.8$, $\Delta H° = 22(2)$ kJ/mol, and $\Delta S° = 88(6)$ J/mol as measured by ^1H NMR. The approach to equilibrium followed first order kinetics as determined by time-resolved UV–visible measurements with $k_f(20\ °C) = 1.1 \times 10^{-4}\ s^{-1}$, $k_r(20\ °C) = 2.3 \times 10^{-5}\ s^{-1}$, $\Delta H_f^{\ddagger} = 78(8)$ kJ/mol, $\Delta S_f^{\ddagger} = 79(10)$ J/mol, $\Delta H_r^{\ddagger} = 56(7)$ kJ/mol, and $\Delta S_r^{\ddagger} = -9(6)$ J/mol. In the absence of added chloride, rapid solvolysis occurs to give *trans*- or *cis*-$[Os(tpy)(Cl)(MeOH)(N)]^{2+}$ as shown by absorption and conductivity measurements. Isomerization does not occur in dichloromethane. A mechanism for isomerization and substitution is proposed involving associative attack of methanol to form seven-coordinate, solvent-bound intermediates which undergo solvolysis by loss of chloride or isomerization by interchange of the chloro and nitrido groups.

Introduction

There is an extensive coordination chemistry of complexes containing the nitrido ligand, which includes $[Os(N)(Cl)_4]^-$, $Re(N)(Cl)_2(PR_3)_2$, and $[Mo(N)(Cl)_4]^-$.[2-8] In these complexes there is often a simple substitutional chemistry at the metal, such as ligand exchange with halides or phosphines without involvement of the nitrido ligand. The strong *trans* effect of the nitrido plays an important role in determining stereochemistry and, presumably, substitution rates.

These and related complexes containing nitrogen ligands may be important as models or stabilized forms of intermediates that play a role in the multiple electron transfer chemistry of nitrogen including nitrite reduction *via* nitrosyls[9-22]

$$[Ru(bpy)_2(py)(NO_2)]^+ + 2\,H^+ \rightleftharpoons [Ru(bpy)_2(py)(NO)]^{3+} + H_2O \quad (1)$$

$$[Ru(bpy)_2(py)(NO)]^{3+} \underset{-\,6e^-,\,-\,5H^+,\,+H_2O}{\overset{+\,6e^-,\,+\,5H^+,\,-H_2O}{\rightleftharpoons}} [Ru(bpy)_2(py)(NH_3)]^{2+} \quad (2)$$

and in the nitrite reductase enzymes.[9,13-22] The redox chemistry of $[Os(tpy)(Cl)_2(N)]^+$ is especially relevant in this regard. It has been shown to undergo reduction to $[Os(tpy)(Cl)_2(NH_3)]$, which is reversible toward reoxidation to $[Os(tpy)(Cl)_2(N)]^+$.[4,23] The redox chemistry has been extended to reactions with phosphines to give phosphoraminato complexes of osmium(IV), $[Os(tpy)(Cl)_2(NPR_3)]^+$.[24]

In this manuscript we describe a new aspect of this coordination chemistry, a *cis/trans* equilibrium, and the quantitative details that characterize it.

Experimental Section

General Details. All synthetic preparations were carried out under ambient conditions. OsO_4 (Alfa), tpy (2,2′;6′,2″-terpyridine, Fluka), $[NBu_4][OH]$ (Aldrich), all solvents (unless otherwise specified) and $[NH_4][PF_6]$ were used as received. $[NBu_4][PF_6]$ (TBAH) was recrystallized three times from boiling ethanol and dried under vacuum at 120 °C for 2 days. $Na[BAr_4]$ (sodium tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate) was prepared according to the literature.[25] NMR spectra were acquired on Bruker AML300 or WM250 spectrometers, and chemical shifts are reported as ppm vs TMS at 20 °C in CD_3OD unless otherwise specified. Deuterated solvents were purchased from CIL and used as received. UV–vis spectra were recorded on an OLIS modified Cary 14 spectrophotometer in 1 cm cuvettes. Analyses were performed by Oneida Research Services.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1994.

(1) National Institutes of Health post-doctoral fellow, 1993–1995.
(2) Wright, M. J.; Griffith, W. P. *Transition Met. Chem. (Weinheim, Ger.)* **1982**, *7*, 53.
(3) Pawson, D.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1975**, 417.
(4) Ware, D. C.; Taube, H. *Inorg. Chem.* **1991**, *30*, 4598.
(5) Griffith, W. P.; Pawson, D. *J. Chem. Soc., Dalton Trans.* **1973**, 1315.
(6) Griffith, W. P. *Coord. Chem. Rev.* **1972**, *8*, 369.
(7) Dehnicke, K.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 955.
(8) Beck, J.; Schweda, E.; Strähle, J. *Z. Naturforsch., B* **1985**, *40*, 1073.
(9) Barley, M. H.; Rhodes, M. R.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 1746.
(10) Keene, F. R.; Salmon, D. J.; Walsh, J. L.; Abruna, H. D.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1896.
(11) Rhodes, M. R.; Meyer, T. J. Unpublished results.
(12) Townsend, R. E.; Coskran, K. J. *Inorg. Chem.* **1971**, *10*, 1661.
(13) Younathan, J. N.; Wood, K. S.; Meyer, T. J. *Inorg. Chem.* **1992**, *31*, 3280.
(14) Lancaster, J. R.; Vega, J. M.; Kamin, H.; Orme-Johnson, N. R.; Orme-Johnson, W. H.; Krueger, R. J.; Siegel, L. M. *J. Biol. Chem.* **1979**, *254*, 1268.
(15) Losada, M. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *104*, 205.
(16) Candau, P.; Manzano, C.; Losada, M. *Nature* **1976**, *262*, 715.
(17) Murphy, W. R.; Takeuchi, K. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 5817.
(18) Murphy, W. R.; Takeuchi, K.; Barley, M. H.; Meyer, T. J. *J. Inorg. Chem.* **1986**, *25*, 1041.
(19) Godwin, J. B.; Meyer, T. J. *Inorg. Chem.* **1971**, *10*, 471.
(20) Bottomley, F.; Mukaida, M. *J. Chem. Soc., Dalton Trans.* **1982**, 1933.
(21) Armor, J. N.; Hoffman, M. *Inorg. Chem.* **1975**, *14*, 444.
(22) Armor, J. *Inorg. Chem.* **1973**, *12*, 1959.
(23) Pipes, D. W.; Bakir, M.; Vitols, S. E.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5507.
(24) Bakir, M.; White, P. S.; Dovletoglou, A.; Meyer, T. J. *Inorg. Chem.* **1991**, *30*, 2836.
(25) Brookhart, M. *Organometallics* **1992**, *11*, 3920.

0020-1669/95/1334-0586$09.00/0

Conductivity Studies. Conductivity measurements were conducted by using a YSI Model 35 conductance meter and a YSI 3402 probe sealed in parafilm and immersed in a flowing water bath with temperature controlled by a circulator. $[N(PPh_3)_2]Cl$, $[Ru(bpy)_3]Cl_2$, and $[Ru(bpy)_3][PF_6]_2$ were used to determine the conductances of 1:1 and 2:1 electrolytes in methanol under these conditions. The background conductance of the solvent alone was less than 10% of the conductance of the samples in all cases. The conductance of the standards was invariant over the timescale of the kinetic experiments.

In a typical kinetic experiment, the electrolyte was added to preequilibrated solvent in the sample cell (volume = 12.0 mL), and the solid dissolved by agitation with a glass pipette. Data collection was begun when the solid was completely dissolved with $t = 0$ taken as the time when the solid was introduced into the solution.

Molar conductivity or specific conductance (Λ) was obtained by the following equations:

$$\bar{L} = K \times L$$

$$\Lambda = \frac{1000L}{[X]}$$

L is the background-subtracted conductance of the solution, $\bar{L}$ is the specific conductance, K is the cell constant (the area of the electrodes divided by the distance between them; a measured constant), and [X] is the concentration of the electrolyte.

Equilibrium and Kinetic Experiments. Equilibrium constants were determined by following the reaction of interest on the Bruker AML300 spectrometer until the ratio *cis–trans* remained constant as shown by integration of the tpy resonances. Probe temperatures were calculated by using the temperature dependent frequency difference between the aliphatic and hydroxyl resonances of methanol or ethylene glycol by the standard method.[26] Rate constants were determined by fitting time-resolved UV–visible spectra by using the global kinetic analysis program SPECFIT.[27] Spectra were recorded on an HP-8452A diode array spectrophotometer with temperature control provided by a water bath circulator. Solutions of the salts were prepared by addition of a weighed amount of salt to temperature preequilibrated solutions of $[N(PPh_3)_2]Cl$ in a 25 mL volumetric flask, with the time base started at the moment of addition of the solid.

Values for $\Delta H°$ and $\Delta S°$ were obtained from plots of ln K vs $1/T$ and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ from plots of ln (k/T) vs $1/T$. Error estimates in $\Delta H°$ and $\Delta S°$ were obtained by assuming a deviation in the value for K by $\pm$ 0.1 (consistent with observed values) and taking lines having the least and greatest slope. Errors in the Eyring plots were from statistical analysis of the data.

Preparation of Compounds. $K_2[OsO_2(OH)_4]$ (Potassium Osmate). This salt was prepared as reported in ref 28. Essentially quantitative yields were obtained routinely.

$[NBu_4][Os(N)(Cl)_4]$. This preparation essentially follows that reported by Griffith and Pawson,[5] but due to the scant details provided there, we describe our procedure here. Potassium osmate (7.18 g, 19.5 mmol) was dissolved in concentrated HCl (200 mL) to give an olive green solution. Sodium azide (2.54 g, 39.0 mmol) in water (10 mL) was added to the stirred solution, causing vigorous effervescence and a gradual color change to brown and then to cherry red. The solution was stirred for 4 h, and 40% $[NBu_4][OH]$ in H_2O (5.24 mL, 20.0 mmol) was added via syringe. Immediately, a pink solid precipitated. After being stirred for 15 min, the slurry was filtered and washed with copious amounts of deionized water, followed by a similar amount of ether. Addition of ether caused the precipitate to turn purple from its initial pink color due to formation of the adduct $[Os(N)(Cl)_4(Et_2O)]^-$, which reverts to the desired product upon air drying. The product was recrystallized from boiling acetone to give 10.3 g (90%) of dark ruby crystals.

***trans*-$[Os(tpy)(Cl)_2(N)]Cl$ (1).** This salt has been prepared previously.[23] We have developed a modified, higher yield procedure. The preparation described here provides high yields of pure material of the formula given. $[NBu_4][Os(N)(Cl)_4]$ (568 mg, 964 μmol) was dissolved in dichloromethane (20 mL) with stirring and tpy (225 mg, 964 μmol) was added. The solution was stirred for at least 5 h, during which time it turned purple and a purple powder precipitated from the solution. It was filtered through a glass frit and washed with copious amounts of dichloromethane to remove $[NBu_4]Cl$, and dried *in vacuo*, affording 475 mg (93%) of a magenta solid. ^1H NMR (CD_3CN): δ 9.04 (d, 6,6″-tpy), 8.62 (d, 3,3″-tpy), 8.50 (dd, 4′-tpy), 8.43 (4,4″-tpy), 8.32 (3′,5′-tpy), 8.02 (ddd, 5,5″). UV–vis (MeOH) [λ_{max} nm (log ϵ)]: 291 (4.19), 338 (3.97), 353 (3.92), 369 (3.76), 514 (2.15).

***trans*-$[Os(tpy)(Cl)_2(N)][PF_6]$ (2).** Salt **1** (1.00 g, 1.89 mmol) was dissolved in methanol (100 mL), and $[NH_4][PF_6]$ (315 mg, 1.89 mmol) was added. A dark pink solid began to precipitate immediately, and the solution was stirred for 5 min. After filtration, the pink solid was washed with cold methanol followed by copious amounts of ether and dried in air to give 885 mg (73%) of a pale purple powder. ^1H NMR (CD_3CN): δ 9.00 (d, 6,6″-tpy), 8.58 (d, 3,3″-tpy), 8.47 (dd, 4′-tpy), 8.41 (4,4″-tpy), 8.32 (3′,5′-tpy), 7.97 (ddd, 5,5″). UV–vis (CH_3CN) [λ_{max} nm (log ϵ)]: 288 (4.15), 336 (3.91), 354 (3.90), 512 (2.56). Anal. Calcd for $C_{15}H_{11}N_4Cl_2PF_6Os$: C, 27.57; H, 1.70; N, 8.58. Found: C, 27.26; H, 1.64; N, 8.63.

***trans*-$[Os(tpy)(Cl)_2(N)][BAr_4]$ (3).** Salt **1** (50 mg, 94 mmol) and $[Na][BAr_4]$ (84 mg, 94 mmol) were slurried in dichloromethane (10 mL) for approximately 2 min with vigorous agitation. The resulting cloudy pink solution was then filtered through celite, leaving a pale brown powder and a transparent solution, which remained unchanged (by UV–vis) after 5 h at room temperature. ^1H NMR (CD_2Cl_2): δ 8.94 (d, 6,6″-tpy), 8.38 (mult, 3,3″-tpy, 4′-tpy, 4,4″-tpy), 8.32 (3′,5′-tpy), 8.02 (ddd, 5,5″). UV–vis (CH_3CN) [λ_{max} nm (log ϵ)]: 298 (4.20), 340 (4.16), 516 (2.38).

***cis*-$[Os(tpy)(Cl)_2(N)][PF_6]$ (4).** A solution of **1** (100 mg, 183 μmol) and LiCl (77 mg, 1.83 mmol) in methanol (25 mL) was prepared at 50 °C and allowed to stir for 30 min, resulting in an orange solution. Ammonium hexafluorophosphate (35 mg, 210 mmol) was added as a solid and the solution cooled to 0 °C for 5 min, after which the orange-brown precipitate was collected by filtration, washed with room temperature methanol and ether, and dried to give 85 mg (71%). ^1H NMR (CD_3CN): δ 9.81 (d, 6,6″-tpy), 8.88 (mult, 4′-tpy), 8.78 (d, 3,3″-tpy, 3′,5′-tpy), 8.68 (td, 4,4″-tpy), 8.19 (ddd, 5,5″). UV–vis (CH_3CN) [λ_{max} nm (log ϵ)]: 278 (4.05), 302 (3.99), 360 (3.98), 372 (3.98). Anal. Calcd for $C_{15}H_{11}N_4Cl_2PF_6Os$: C, 27.57; H, 1.70; N, 8.58. Found: C, 27.71; H, 1.61; N, 8.44.

***cis*-$[Os(tpy)(Cl)_2(N)][BAr_4]$ (5).** Salt **4** (20 mg, 31 μmol) and $Na[BAr_4]$ (27 mg, 31 μmol) were slurried in dichloromethane (5 mL) for approximately 2 min with vigorous agitation. The resulting cloudy orange solution was filtered through Celite, leaving a pale brown powder and a transparent solution, which remained unchanged (by UV–vis) after 5 h at room temperature. ^1H NMR (CD_2Cl_2): δ 9.95 (d, 6,6″-tpy), 8.77 (mult, 4′-tpy), 8.63 (td, 4,4″-tpy), 8.57 (d, 3,3″-tpy, 3′,5′-tpy), 8.21 (ddd, 5,5″). UV–vis (CH_3CN) [λ_{max} nm (log ϵ)]: 270 (4.38), 278 (4.37), 306 (4.26), 354 (4.19), 370 (4.14), 456 (2.55).

Results

Syntheses. In our hands, the sole product of reaction between $[NBu_4][Os(N)(Cl)_4]$ and 2,2′:6′,2″-terpyridine (tpy) in dichloromethane is $[Os(tpy)(Cl)_2(N)]Cl$ (**1**), eq 3.[23] This salt is

$$[NBu_4][Os(N)(Cl)_4] + tpy \rightarrow trans\text{-}[(tpy)(Cl)_2Os{\equiv}N]Cl + [NBu_4]Cl \quad (3)$$

obtained as a brick red to magenta colored solid, depending on particle size. We have previously structurally characterized **1** and found it to have the tpy ligand *trans* to the nitride.[23] When it is dissolved in potentially ligating solvents (such as methanol or water), a reaction occurs as evidenced by changes in NMR (Figure 1) and absorption[23] spectra (Figure 2).

With added chloride in methanol the reaction observed is equilibration with the tan-colored isomer, *cis*-$[Os(tpy)(Cl)_2(N)]^+$ (eq 4). Analytical data for the *cis* and *trans* salts are identical.

$$trans\text{-}[(tpy)(Cl)_2Os{\equiv}N]^+ \underset{k_r}{\overset{k_f}{\rightleftharpoons}} cis\text{-}[(tpy)(Cl)_2Os{\equiv}N]^+ \quad (4)$$

That there is a structural difference between the two is clear by

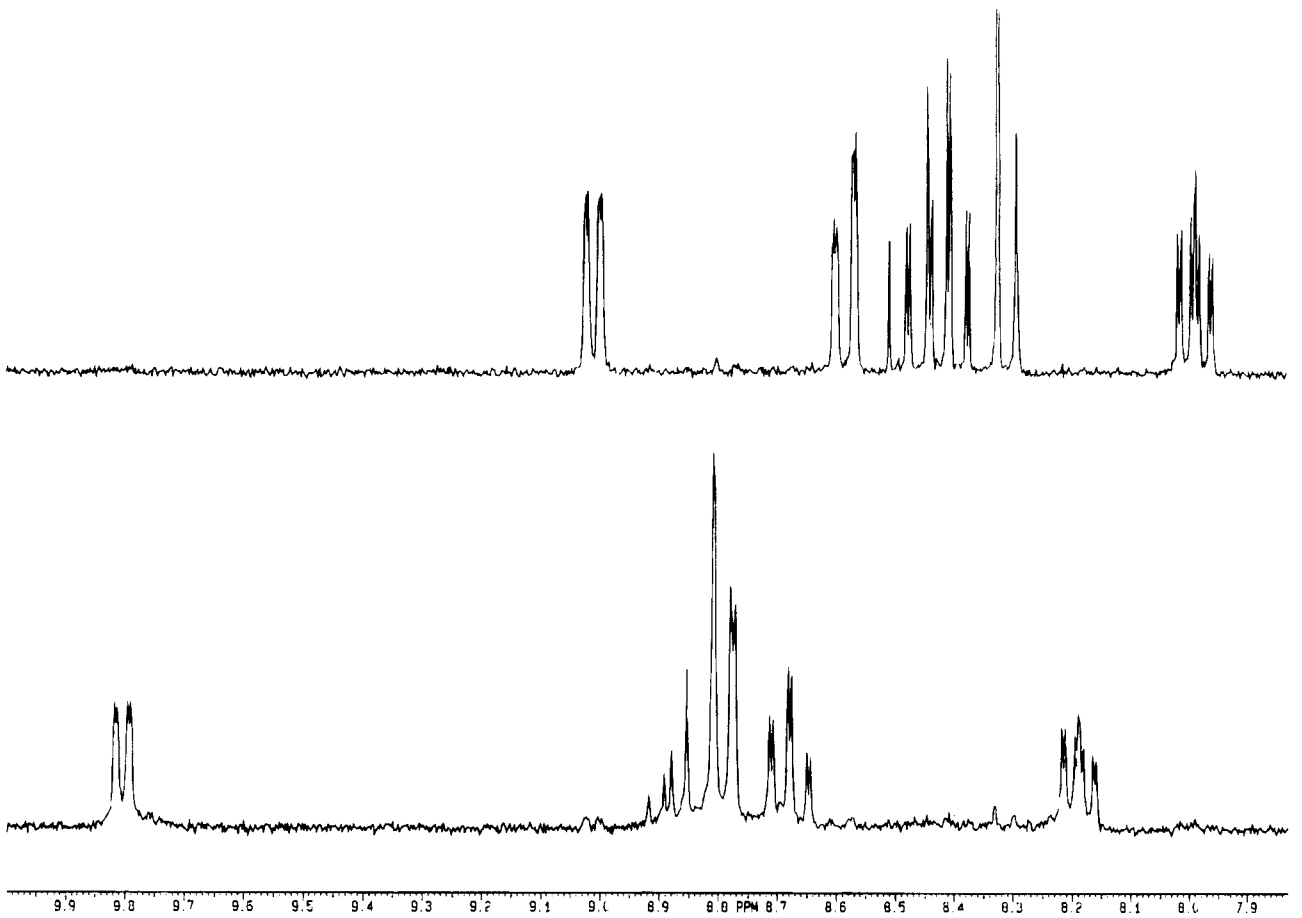


Figure 1. ^{1}H NMR spectra in CD_3CN of (a) *trans*-$[Os(tpy)(Cl)_2(N)][PF_6]$ and (b) *cis*-$[Os(tpy)(Cl)_2(N)][PF_6]$.

the ^{1}H NMR spectra in Figure 1. The resonance of the (magnetically equivalent) ortho protons (6, 6″) on the outer rings of the tpy ligand is sensitive to stereochemistry. In CD_3CN they appear at 9.0 ppm in the *trans* isomer and at 9.8 ppm in *cis*. The large downfield shift in the *cis* isomer is probably due to less effective shielding by electron density in the filled d_{xy} orbital (taking the z axis to lie along the Os−N bond) compared to shielding in *trans* by the in-plane osmium−nitrogen π bond. The other resonances change as well, but not as dramatically.

Other salts of these cations are readily prepared by metathesis. As reported previously, *trans*-$[Os(tpy)(Cl)_2(N)][PF_6]$ (**2**) precipitates in high yield upon addition of $[NH_4][PF_6]$ to a methanolic solution of *trans*-$[Os(tpy)(Cl)_2(N)]Cl$.[23] In order to prepare a salt with the anion tetrakis{3,5-bis(trifluoromethyl)-phenyl}borate (abbreviated $[BAr_4]^-$) it was necessary to slurry **1** with the sodium salt in dry dichloromethane to achieve complete metathesis. Filtration cleanly removes NaCl from the resulting solution of **3**. Similarly, a solution containing *cis*-$[Os(tpy)(Cl)_2(N)][BAr_4]$ (**5**) could be prepared from **4**. Due to the instability of the nitrido complexes at high concentrations[23,29] and the oily nature of the $[BAr_4]^-$ salts, it was impossible to isolate them as solids from these solutions. Significantly, no isomerization is observed in CH_2Cl_2.

Absorption Spectra. As shown by the data in Figure 3, absorption spectra of the *cis* and *trans* isomers in acetonitrile are different and both are solvent dependent. Spectral features are summarized in Table 1. The d^2 configuration of these complexes gives rise to LaPorte forbidden, $d\pi \rightarrow d\pi$ transitions in the visible region with $\epsilon < 300$ M^{-1} cm^{-1}. Intense absorptions ($\epsilon > 10^3$) appear in the UV due to structured, solvent-dependent LMCT bands.[30-37] Ligand-localized $\pi \rightarrow \pi^*$ (tpy) bands appear below ~310 nm. These bands are not highly solvent dependent and the pattern is significantly different between *trans* and *cis*. The data in methanol were acquired with added chloride to suppress solvolysis (see below).

Isomerization. Changes in UV−visible spectra of *trans*-$[Os(tpy)(Cl)_2(N)][PF_6]$ in methanol over a period of hours are shown in Figure 2 and final spectra with and without added Cl^- in Figure 4. Over this period there is a decrease in absorption at λ_{max} 325 nm, and an increase at 344 nm. There are no true isosbestic points during the reaction if chloride is not added. Over even longer periods a decomposition reaction occurs (presumably from coupling to form dinitrogen and

(26) VanGeet, A. L. In *Abstracts of the 10th Experimental NMR Conferences*; Mellon Institute: Pittsburgh, PA, March, 1969.
(27) Binstead, R. B.; Zuberbühler, A. D., SPECFIT, ver. 1.1, Spectrum Software Associates, 1993.
(28) Malin, J. M. *Inorg. Synth.* **1980**, *20*, 61.
(29) Ware, D. C.; Taube, H. *Inorg. Chem.* **1991**, *30*, 4605.
(30) Che, C.-M.; Lau, T.-C.; Lam, H.-W.; Poon, C.-K. *J. Chem. Soc., Chem. Commun.* **1989**, 114.
(31) Che, C.-M.; Lam, H.-W.; Tong, W.-F.; Lai, T.-F.; Lau, T.-C. *J. Chem. Soc., Chem. Commun.* **1989**, 1883.
(32) Che, C.-M.; Lam, H.-W.; Mak, C. W. *J. Chem. Soc., Chem. Commun.* **1989**, 1529−31.
(33) Collison, D.; Garner, C. D.; Mabbs, F. E.; King, T. J. *J. Chem. Soc., Dalton Trans.* **1981**, 1820.
(34) Collison, D.; Garner, C. D.; Mabbs, F. E.; Salthouse, J. A.; King, T. J. *J. Chem. Soc., Dalton Trans.* **1981**, 1812.
(35) Lam, H. W.; Chin, K. R.; Che, C. M.; Wang, R. J.; Mak, T. C. *Inorg. Chim. Acta* **1993**, *204*, 133.
(36) Cowman, C. D.; Trogler, W. C.; Mann, K. R.; Poon, C. K.; Gray, H. B. *Inorg. Chem.* **1976**, *15*, 1747.
(37) Hopkins, M. D.; Miskowski, V. M.; Gray, H. B. *J. Am. Chem. Soc.* **1986**, *108*, 6908.

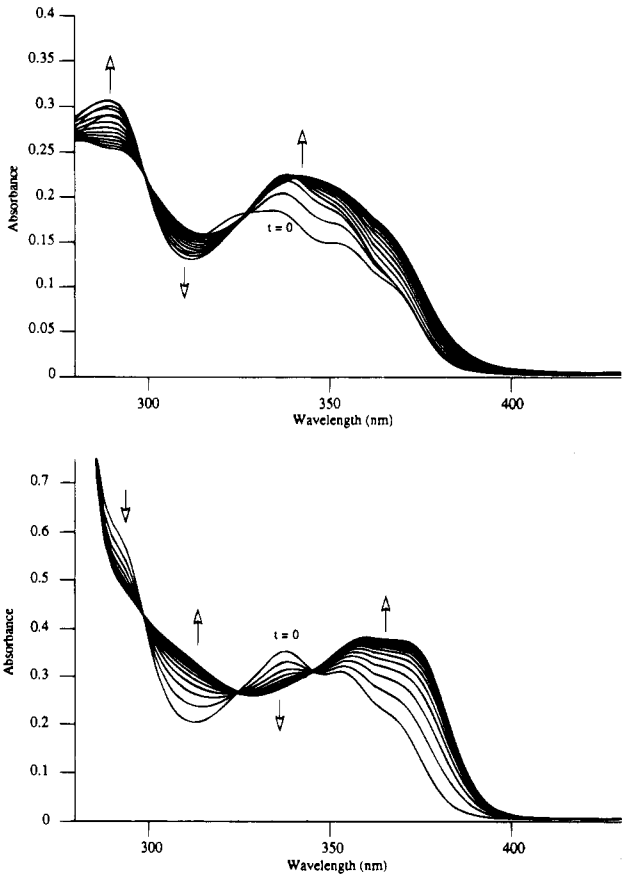


Figure 2. Spectral changes at 10 min intervals after dissolution of *trans*-$[Os(tpy)(Cl)_2(N)][PF_6]$, 10^{-4} M, in MeOH in a 1 cm cell at 14.5 °C, with 0 M chloride (above) and with 10^{-3} M chloride (below).

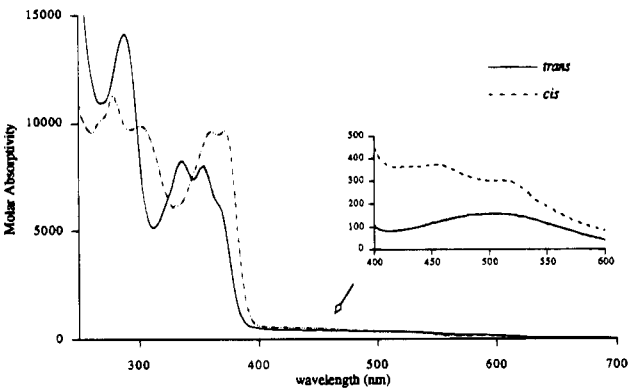


Figure 3. Absorption spectra of *trans*-$[Os(tpy)(Cl)_2(N)][PF_6]$ and *cis*-$[Os(tpy)(Cl)_2(N)][PF_6]$ in acetonitrile.

Os^{III}).[29] When *trans*-$[Os(tpy)(Cl)_2(N)][PF_6]$ is dissolved in MeOH with a 10-fold excess of added $[N(PPh_3)_2]Cl$, similar spectral changes occur but with isosbestic points at 298, 324, and 345 nm. The final spectrum is consistent with a convoluted mix of *cis*- and *trans*-$[Os(tpy)(Cl)_2(N)]^+$. Both *trans*-$[Os(tpy)(Cl)_2(N)]^+$ and *cis*-$[Os(tpy)(Cl)_2(N)]^+$ are stable toward isomerization in dichloromethane.

In attempts to identify a solvento intermediate in methanol, NMR spectra of **1** in CD_3OD were obtained at various times during the reaction by chilling the solution to as low as −90 °C (methanol calibration). However, only one set of resonances was present, even in samples prepared immediately prior to spectral acquisition. At no temperature were we able to observe distinct sets of resonances for dichloro and solvento complexes, only sets of averaged resonances for *trans* or *cis* were observed.

Table 1. UV−Visible Data

cation	solvent	λ_{max} (nm)	log ϵ^a	assignment
trans-$[Os(tpy)(Cl)_2(N)]^+$	CH_2Cl_2	270	4.38	tpy ($\pi \rightarrow \pi^*$)
		280	4.32	tpy ($\pi \rightarrow \pi^*$)
		292	4.29	tpy ($\pi \rightarrow \pi^*$)
		340	4.16	LMCT (N → Os)
		520	2.1	$d\pi \rightarrow d\pi$
	CH_3CN	288	4.17	tpy ($\pi \rightarrow \pi^*$)
		336	3.94	tpy ($\pi \rightarrow \pi^*$)
		354	3.93	LMCT (N → Os)
		366	3.83	LMCT (N → Os)
		514	2.1	$d\pi \rightarrow d\pi$
	CH_3OH^b	289	4.18	tpy ($\pi \rightarrow \pi^*$)
		328	3.98	tpy ($\pi \rightarrow \pi^*$)
		334	3.99	tpy ($\pi \rightarrow \pi^*$)
		350	3.87	LMCT (N → Os)
		366	3.69	LMCT (N → Os)
		514	2.1	$d\pi \rightarrow d\pi$
cis-$[Os(tpy)(Cl)_2(N)]^+$	CH_2Cl_2	272	4.38	tpy ($\pi \rightarrow \pi^*$)
		280	4.37	tpy ($\pi \rightarrow \pi^*$)
		306	4.26	tpy ($\pi \rightarrow \pi^*$)
		354	4.19	LMCT (N → Os)
		370	4.14	LMCT (N → Os)
		456	2.55	$d\pi \rightarrow d\pi$
	CH_3CN	268	4.02	tpy ($\pi \rightarrow \pi^*$)
		280	4.07	tpy ($\pi \rightarrow \pi^*$)
		302	4.02	tpy ($\pi \rightarrow \pi^*$)
		360	4.01	LMCT (N → Os)
		372	4.01	LMCT (N → Os)
		460	2.45	$d\pi \rightarrow d\pi$
	CH_3OH^b	292	4.04	tpy ($\pi \rightarrow \pi^*$)
		344	4.01	LMCT (N → Os)
		470	2.4	$d\pi \rightarrow d\pi$

[a] ϵ in units of M^{-1} cm^{-1}. [b] With 10-fold added chloride to supress solvolysis.

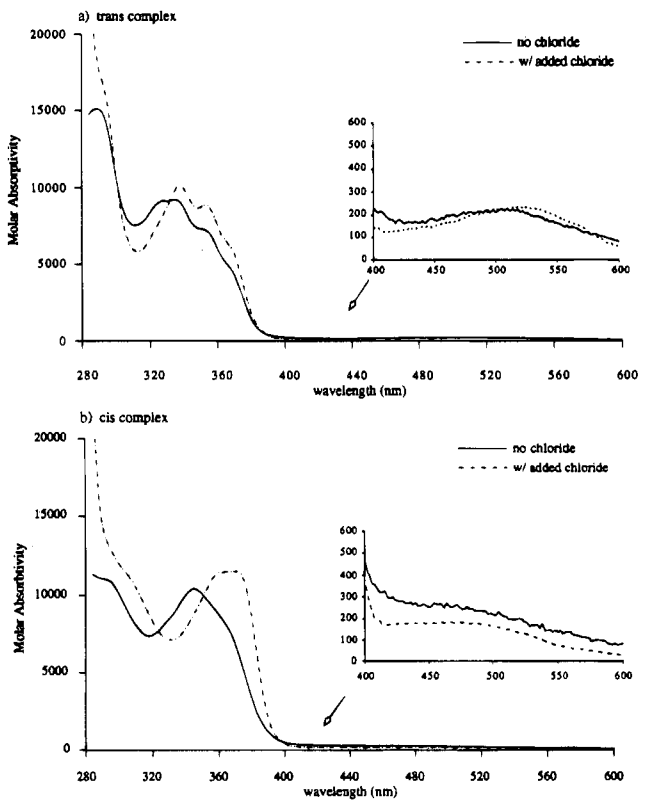


Figure 4. Absorption spectra of (a) *trans*-$[Os(tpy)(Cl)_2(N)][PF_6]$ and (b) *cis*-$[Os(tpy)(Cl)_2(N)][PF_6]$ in methanol with added chloride and without added chloride.

Conductivity studies were conducted on solutions of the *cis* and *trans* salts in methanol at 25 °C. Estimates of the molar

Table 2. Molar Conductivities (Λ) in Methanol at 25 °C

salt	salt concn (M)	L_{cor} (Ω^{-1})[a]	Λ (Ω^{-1} mol^{-1})[a]
$[N(PPh_3)_2]Cl$	1.6×10^{-4}	1.04×10^{-4}	65(6)
	1.81×10^{-3}	1.18×10^{-3}	65.1(5)
	1.28×10^{-3}	7.91×10^{-4}	61.9(9)
$[Ru(bpy)_3]Cl_2$	7.42×10^{-4}	9.63×10^{-4}	130(3)
$[Ru(bpy)_3][PF_6]_2$	1.84×10^{-4}	2.42×10^{-4}	131(5)
trans-$[Os(tpy)(Cl)_2(N)]Cl$	1.7×10^{-4}	9.5×10^{-5}	56(5)[b]
	1.29×10^{-3}	7.95×10^{-4}	61.7(7)[b]
	2.18×10^{-3}	1.31×10^{-3}	60.0(4)[b]
trans-$[Os(tpy)(Cl)_2(N)][PF_6]$	1.79×10^{-4}	1.07×10^{-5}	59.9(5)[b]
cis-$[Os(tpy)(Cl)_2(N)]Cl$	2.61×10^{-4}	1.06×10^{-5}	63.8(18)[b]
cis-$[Os(tpy)(Cl)_2(N)][PF_6]$	1.66×10^{-4}	1.8×10^{-5}	63.9(5)[b]

[a] L_{cor} and Λ are the background-subtracted solution conductance and specific conductance of the electrolyte, respectively. [b] The initial value acquired at $t < 20$ s.

conductivities of 1:1 and 2:1 electrolytes under these conditions were obtained from measurements on solutions containing $[N(PPh_3)_2]Cl$, $[Ru(bpy)_3]Cl_2$, and $[Ru(bpy)_3][PF_6]_2$. These salts were chosen because of the commonality of their anions and the similarities of their molecular weights with the nitrido salts.

In Table 2 are listed molar conductivities (Λ) for the standards and initial values for salts of the *cis* and *trans* isomers. Plots of Λ vs time for the *trans* and *cis* $[PF_6]^-$ and Cl^- salts are shown in Figure 5. For all four salts, the initial value of Λ is nearly that for a 1:1 electrolyte, but Λ increases with time. For both the *cis* and *trans* PF_6^- salts, ionization continues until the conductivity reaches a value consistent with nearly complete formation of a 2:1 electrolyte. These observations are consistent with rapid solvolysis of the *cis* and *trans* isomers to give the corresponding solvento complexes, reactions 5 and 6, with the

$$\textit{trans}\text{-}[Os(tpy)Cl_2(N)]^+ + MeOH \rightleftharpoons \textit{trans}\text{-}[Os(tpy)Cl(MeOH)(N)]^{2+} + Cl^- \quad (5)$$

$$\textit{cis}\text{-}[Os(tpy)Cl_2(N)]^+ + MeOH \rightleftharpoons \textit{cis}\text{-}[Os(tpy)Cl(MeOH)(N)]^{2+} + Cl^- \quad (6)$$

equilibria lying largely to the right. The equilibria must be facile since only the dichloro complexes could be isolated from the solutions with addition of PF_6^-.

On the basis of the conductivity and spectral changes, loss of chloride from either the *cis* or *trans* isomer is rapid. Equilibration between *cis* and *trans* solvento complexes, eq 7

$$\textit{trans}\text{-}[Os(tpy)(Cl)(MeOH)(N)]^{2+} \rightleftharpoons \textit{cis}\text{-}[Os(tpy)(Cl)(MeOH)(N)]^{2+} \quad (7)$$

is far slower. The initial *trans* and *cis* geometries of the dichloro complexes must be retained in the solvento complexes. From the data in Figure 5 the conductivities increase with time for the chloride salts at comparable rates but to a far lesser degree. This is consistent with the conclusion reached above with the small amount of chloride added acting to suppress the equilibria in reactions 5 and 6. Isomerization continues to occur but with the *cis*- and *trans*-dichloro complexes as the dominant forms.

Equilibrium constants for *trans*−*cis* isomerization in methanol with added chloride were determined at three temperatures by measuring the ratio of the ^1H NMR resonances for the 6,6″ protons of the two isomers after equilibrium had been reached. The results are given in Table 3. K was independent of the concentrations of either the osmium complex or chloride, consistent with eq 4. Values were unobtainable above 30 °C due to decomposition of the *cis* isomer. The values at higher

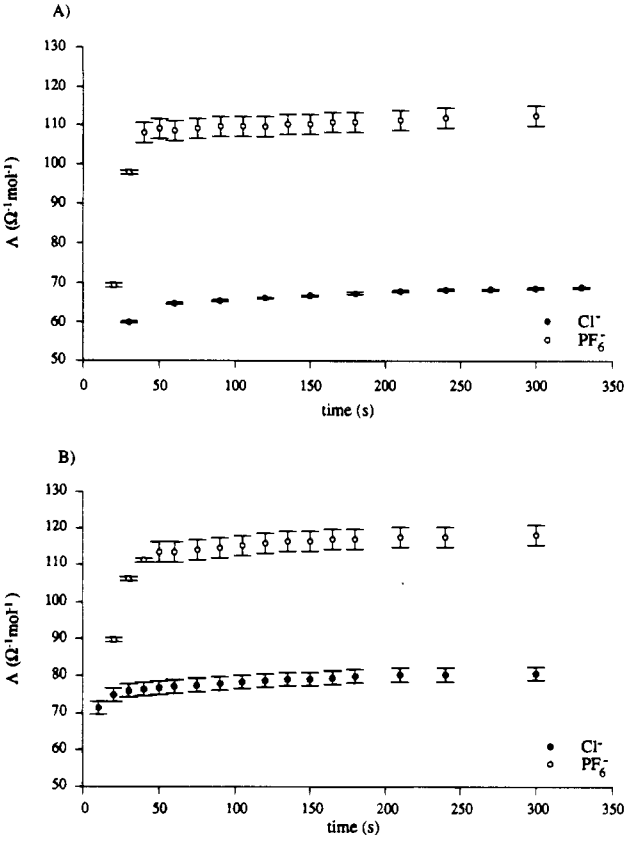


Figure 5. Molar conductivities (Λ) as a function of time for (A) *trans*-$[Os(tpy)(Cl)_2(N)]^+$ and (B) *cis*-$[Os(tpy)(Cl)_2(N)]^+$ in methanol at 25 °C.

Table 3. Rate and Equilibrium Constants in Methanol for *Trans*−*Cis* Isomerization in $[Os(tpy)(Cl)_2(N)]^+$

temp (°C)	10^5[Os] (M)	10^5[Cl$^-$] (M)	K	k_{obs} (s^{-1})	k_f (s^{-1})[a]	k_r (s^{-1})[a]
50.0	16.8	1700	11[b]	25×10^{-4}	23×10^{-4}	21×10^{-5}
	15.9	160		24×10^{-4}	22×10^{-4}	20×10^{-5}
40.0	3.5	350	8.5[b]	10×10^{-4}	90×10^{-5}	11×10^{-5}
	3.5	350		98×10^{-5}	88×10^{-5}	10×10^{-5}
30.0	16.4	1600	6.4	39×10^{-5}	34×10^{-5}	5.3×10^{-5}
	3.5	350		36×10^{-5}	31×10^{-5}	4.9×10^{-5}
20.3	3.5	350	4.8	13×10^{-5}	11×10^{-5}	2.3×10^{-5}
	3.5	350		13×10^{-5}	11×10^{-5}	2.3×10^{-5}
14.5	2.6	260	4.0	6.9×10^{-5}	5.5×10^{-5}	1.4×10^{-5}
	20.0	2000		7.4×10^{-5}	5.9×10^{-5}	1.5×10^{-5}
	19.9	200		7.1×10^{-5}	5.7×10^{-5}	1.4×10^{-5}

[a] Calculated from the experimentally observed first-order rate constant k_{obs} and $k_{obs} = k_f + k_r$, $K = k_f/k_r$. [b] Calculated by using eq 8.

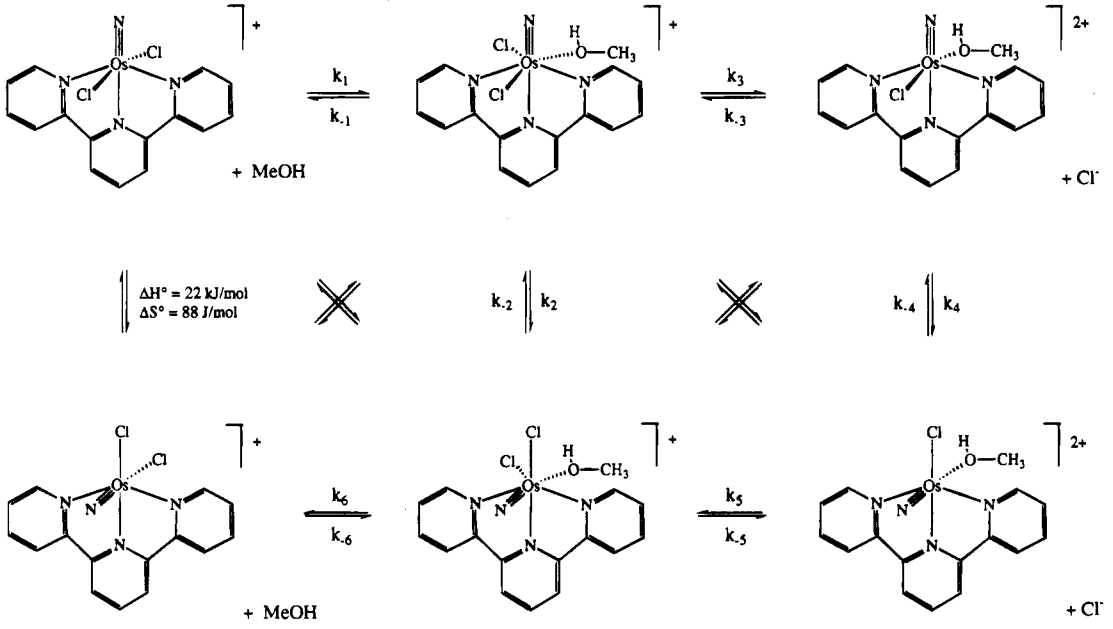
temperatures in Table 3 were calculated from the van't Hoff equation in the form

$$\ln K = (11 \pm 1) - (2600 \pm 200)T^{-1} \; (r^2 = 0.999) \quad (8)$$

which gave $\Delta H° = 22 \pm 2$ kJ/mol and $\Delta S° = 88 \pm 6$ J/mol.

Kinetics. Rate constants for *trans*−*cis* isomerization in methanol were obtained by UV−visible measurements. Solutions of *trans*-$[Os(tpy)(Cl)_2(N)]^+$ in methanol were prepared immediately prior to use with the solvent preequilibrated at the temperature used for data collection. The *trans*:*cis* ratio was unaffected by variations in [Cl$^-$] at least up to 0.01 M as shown by ^1H NMR. Similarly, the rates of the forward and reverse reactions were [Cl$^-$] independent up to at least 0.01 M. The kinetics were conducted at chloride concentrations sufficiently high (10-fold excess over osmium) that the solvento complexes were unobservable, and isosbestic behavior at 298, 324, and

Scheme 1



345 nm was obtained. Data obtained with a 100-fold excess of added PF_6^- were indistinguishable from those without added PF_6^-.

The kinetic data were modeled as a first order approach to equilibrium consistent with eq 4 by using the program Specfit.[27] Values of K were obtained from ^1H NMR data below 35 °C, and by extrapolation above this temperature. The individual rate constants were calculated from the relations

$$k_{obs} = k_f + k_r$$

$$K = k_f/k_r$$

where k_{obs} was the experimentally observed, first-order rate constant. Factor analysis was used to determine the number of species present in the solution, with two, the *cis* and *trans* isomers, being sufficient to account for the spectral changes with a 10-fold excess of chloride. A global least squares minimum was obtained at all wavelengths in each spectrum by using a Marquardt fit to the data with the assumption of two species.

Eyring plots of $\ln(k/T)$ vs $1/T$ were linear for k_f and k_r over the temperature range 14.5–50 °C and gave $\Delta H_f^{\ddagger} = 78 \pm 1$ kJ/mol (18.6 kcal/mol), $\Delta S_f^{\ddagger} = 79 \pm 5$ J/mol (18.9 cal/(mol deg)), $\Delta H_r^{\ddagger} = 56 \pm 2$ kJ/mol (13.4 kcal/mol), and $\Delta S_r^{\ddagger} = -9 \pm 5$ J/mol (2.2 cal/(mol deg)).

Discussion. Our results show that there are two isomers of $[Os(tpy)(Cl)_2(N)]^+$. The *trans* isomer is the product of the reaction between $[Bu_4N][Os(N)Cl_4]$ and tpy in CH_2Cl_2. The existence of the isomerization was a source of confusion in earlier work. In retrospect, interconversion between $[Os^{VI}(tpy)(Cl)_2(N)]^+$ and $[Os^{II}(tpy)(Cl)_2(NH_3)]$ reported earlier involved the *cis* isomer and not *trans* because of *trans* → *cis* conversion in water.[4,23] The reported conversion of the η^2 complex $[Os(\eta^2\text{-tpy})(Cl)_3(N)]$ to the *trans* isomer may have been the *trans* → *cis* isomerization reported here.[4] When *cis* or *trans*-$[Os(tpy)(Cl)_2(N)]^+$ are dissolved in methanol, rapid solvolysis reactions occur to give the corresponding solvento complexes, eqs 5 and 6. These reactions are evidenced by the changes that occur in UV–visible spectra and in molar conductivities upon dissolution of the PF_6^- salts in methanol, Figures 2 and 5. They were not studied quantitatively but the qualitative dependence of the distribution between species on $[Cl^-]$ is consistent with the equilibria in eqs 4 and 5. Over a longer timescale, *trans*–*cis* isomerization occurs but because of the complexity of the system, no attempt was made to study it quantitatively.

Both *cis*- and *trans*-$[Os(tpy)(Cl)_2(N)]^+$ are stable to isomerization in CH_2Cl_2. Isomerization does occur if methanol is added to CH_2Cl_2. By inference, a potentially coordinating solvent (CH_3CN, CH_3OH, H_2O) is required in order for isomerization to occur. With sufficient added chloride (a 10-fold excess over complex) solvolysis is completely suppressed, *cis*- and *trans*-$[Os(tpy)(Cl)_2(N)]^+$ are the dominant forms in solution, and yet, *trans*–*cis* isomerization continues to occur. Under these conditions the experimentally observed, first-order rate constant is independent of added chloride, at least to 0.01 M.

Given the requirement of a potentially coordinating solvent and the absence of a chloride dependence, the most reasonable mechanism for substitution is by an associative pathway with coordination expansion, in methanol by the addition of methanol, Scheme 1. There is precedence for such intermediates in the d^0 complex of Mo^{VI}, $Mo(tpy)(Cl)(N_3)_2(N)$, which contains the tpy ligand.[8] The geometry of this complex accommodates the nitrido ligand in an axial position *cis* to tpy and the two azide ligands, and *trans* to chloride in a pentagonal bipyramidal structure.

As illustrated in Scheme 1, if isomerization occurs through a seven-coordinate intermediate, it must proceed *via* interchange of the nitrido and chloro ligands followed by loss of methanol. An appealing feature of invoking such intermediates is that they provide a common mechanistic basis for both *trans*–*cis* isomerization and substitution. Loss of chloride or methanol without nitrido–chloro interchange results in either solvolysis or no net change and provides a basis for achieving the equilibria in eqs 4 and 5. These interconversions are rapid. The slow step in either direction is intramolecular rearrangement and nitrido–chloro interchange via the seven-coordinate intermediates. There is no kinetic or spectroscopic evidence to suggest that the seven-coordinate intermediates build up appreciably in solution.

At low or no added chloride all four components, *cis*- and *trans*-$[Os(tpy)(Cl)_2(N)]^+$ and *cis*- and *trans*-$[Os(tpy)(Cl)(MeOH)(N)]^{2+}$ are present and, as noted above, the kinetics are difficult

to interpret. There may be multiple pathways for *trans*–*cis* isomerization in *trans*-$[Os(tpy)(Cl)MeOH)(N)]^{2+}$ as suggested by Scheme 1. If direct isomerization of $[Os(tpy)(Cl)(MeOH)(N)]^{2+}$ plays a role, k_4, k_{-4}, it may occur *via* the seven-coordinate intermediates, *cis*- and *trans*-$[Os(tpy)Cl(MeOH)_2(N)]^{2+}$.

With excess chloride, isomerization occurs through the dichloro complexes. Under these conditions the experimental rate constants k_f and k_r in Table 3 are related to the constants in the Scheme by

$$k_f = k_2K_1 \ (K_1 = k_1/k_{-1})$$

$$k_r = k_{-2}K_6^{-1} \ (K_6 = k_6/k_{-6})$$

With this interpretation the experimental rate constants (k_f, k_r) and activation parameters ($\Delta H_f^{\ddagger}$, $\Delta H_r^{\ddagger}$ and $\Delta S_f^{\ddagger}$, $\Delta S_r^{\ddagger}$) are composite quantities reflecting both preequilibrium and isomerization steps.

In the equilibrium between *trans*- and *cis*-$[Os(tpy)(Cl)_2(N)]^+$ in eq 4, *cis* is favored entropically (ΔS° = 88 J/mol) and disfavored enthalpically (ΔH° = 22 kJ/mol). There is evidence for significant differences between in- and out-of-plane electronic coupling between tpy and nitrido by the differences that appear in the patterns of tpy-based $\pi \rightarrow \pi^*$ bands in the near-UV region, Figure 2 and Table 1. The lowest energy $\pi \rightarrow \pi^*$ band is shifted ca. 2000 cm^{-1} to higher energy in the *trans* complex. This may arise from differences in π(tpy)–dπ–p(N) and/or dπ^*–π^*(tpy) mixing between the in- and out-of-plane nitridos. A contribution to the positive ΔH° for the equilibrium may come from a loss of π electronic coupling in the *cis* isomer.

The entropic change should be dominated by solvent. From the positive value for ΔS° it can be inferred that *trans* → *cis* isomerization results in a decrease in complex–solvent interactions. This is somewhat surprising since the isomerization is accompanied by a decrease in symmetry and, by inference, an increase in electrostatic asymmetry. Specific solvent interactions with the nitrogen atom of the nitrido may play an important role.

Acknowledgment. D.S.W. thanks the National Institutes of Health for National Research Service Award No. 1 F32 GM16282-01. The authors thank Dr. Dave Thompson for helpful discussions. This research was supported by the National Institutes of Health, Grant No. 5-R01-GM32296-06.

IC940298S