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Synthesis of Nitrosylruthenium Complexes Containing 2,2′:6′,2″-Terpyridine by Reactions of Alkoxo Complexes with Acids

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Nitrosylruthenium complexes containing 2,2′:6′,2″-terpyridine (terpy) have been synthesized and characterized. The three alkoxo complexes *trans*-(NO, OCH_3), *cis*-(Cl, OCH_3)-[$RuCl(OCH_3)(NO)(terpy)$]PF_6 ([**2**]PF_6), *trans*-(NO, OC_2H_5), *cis*-(Cl, OC_2H_5)-[$RuCl(OC_2H_5)(NO)(terpy)$]PF_6 ([**3**]PF_6), and [$RuCl(OC_3H_7)(NO)(terpy)$]PF_6 ([**4**]PF_6) were synthesized by reactions of *trans*-(Cl, Cl), *cis*-(NO, Cl)-[$RuCl_2(NO)(terpy)$]PF_6 ([**1**]PF_6) with $NaOCH_3$ in CH_3OH, C_2H_5OH, and C_3H_7OH, respectively. Reactions of [**3**]PF_6 with an acid such as hydrochloric acid and trifluoromethansulforic acid afford nitrosyl complexes in which the alkoxo ligand is substituted. The geometrical isomer of [**1**]PF_6, *trans*-(NO, Cl), *cis*-(Cl, Cl)-[$RuCl_2(NO)(terpy)$]PF_6 ([**5**]PF_6), was obtained by the reaction of [**3**]PF_6 in a hydrochloric acid solution. Reaction of [**3**]PF_6 with trifluoromethansulforic acid in CH_3CN gave *trans*-(NO, Cl), *cis*-(CH_3CN, Cl)-[$RuCl(CH_3CN)(NO)(terpy)$]$^{2+}$ ([**6**]$^{2+}$) under refluxing conditions. The structures of [**3**]PF_6, [**4**]PF_6·CH_3CN, [**5**]CF_3SO_3, and [**6**]$(PF_6)_2$ were determined by X-ray crystallograpy.

Introduction

Nitrogen monoxide coordinates to a metal center with multiple bonds between them.[1,2] There is a strong electronic interaction between the nitrosyl ligand and the metal center. Relationship between the coordination mode and reactivity of the nitrosyl ligand and reactions at the nitrosyl, the metal center, and other ligands of the formed complexes are of interest. Recently, many studies have been reported from a fundamental inorganic and bioinorganic chemistry perspective in connection with the biological functions of nitrogen monoxide.[2−25] The Enemark−Feltham notation, $\{M(NO)_x\}^n$, where n is the sum of the numbers of electrons in the d orbitals of the metal (M) and the π^* orbital of NO, is used for the classification of the structure and bond character between a metal and NO.[7] Many studies on synthesis and properties of nitrosylruthenium complexes that are classified as the $\{Ru(NO)\}^6$ type have been performed.[8−25] These nitrosyl ligands show a strong π-accepting property and are affected by other coexisting ligands through the ruthenium center. It is well-known that the nitrosyl ligand shows a strong interaction with the ligand at the trans position by sharing the same d orbital (trans effect and trans strengthening).[19] Variations in the stretching vibrational mode, redox

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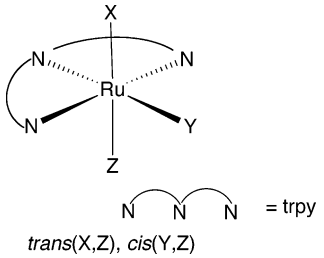
potential, and structural parameters of the (RuNO) moiety in some ruthenium complexes can be explained by variations in the electronic state of the (RuNO) moiety and interactions between the nitrosyl ligand and other coexisting ligands through the metal center and relate to the reactivity of the nitrosyl ligand. Reactions of the nitrosyl ligand of ruthenium complexes showing a high electrophilicity with nucleophiles have been reported.[9,11,18,20,21] On the other hand, low-electrophilic nitrosyl complexes react with Lewis bases at the metal center; substitution reactions of the coexisting ligands and changes of geometry around the central metal (isomerization reaction) are observed to give alternative

Chart 1. Geometrical Configuration of the Complexes



trans(X,Z), *cis*(Y,Z)

nitrosyl complexes.[22] In studies on {RuNO}^{6}-type nitrosyl complexes containing polypyridine ligands, $[Ru(NO)XL_4]^{n+}$ [X = Cl, NO_2, ONO, etc.; L = py (pyridine), $^1/_2$bpy (2,2′-bipyridine), $^1/_2$pyca (2-pyridinecarboxylato)], physical, structural, and redox properties have been elucidated.[10a,b,21−24] In the case of $[Ru(NO)X(pyca)_2]^{n+}$ complexes having six geometrical isomers, we have reported that nature of the X ligand is important for the stability of the isomers; the reactivities and stabilities of isomers containing X ligands with different electronic and structural characters have been evaluated by synthetic and theoretical methods.[22a] We have also reported the synthesis of a nitrosylruthenium complex containing a planar π-accepting tridentate 2,2′:6′,2″-terpyridine (terpy) ligand, *trans*-(Cl, Cl), *cis*-(NO, Cl)-$[RuCl_2(NO)(terpy)]^+$ ($[\mathbf{1}]^+$), whose geometrical configuration notation is shown as Chart 1, as well as its reactions with nucleophiles.[25]

Although the reaction of $[\mathbf{1}]^+$ with azide ion forms a solvated complex with N_2 and N_2O evolution in a manner similar to a well-known characteristic reaction of nitrosyls, a substitution reaction of a chloro ligand occurs in reactions with nitrite and methoxide ions accompanied by a geometrical change around the ruthenium center in which the nitrosyl ligand at the equatorial position with respect to the terpy ligand moves to the axial position. Recently, van Eldik et al. reported the synthesis and spectroscopic characterization of the cis [*trans*-(Cl, NH_3), *cis*-(NH_3, NH_3)] and trans [*trans*-(NH_3, NH_3), *cis*-(Cl, NH_3)] isomers of $[RuCl(NH_3)_2(terpy)](PF_6)_2$ and the reactions of these complexes with NO in connection with the π-accepting properties of the terpy ligand.[13] Reedijk et al. reported the synthesis of an isomer of $[\mathbf{1}]^+$,[12] and many ruthenium complexes containing the terpy ligand and its derivatives have been investigated for their chemical and photochemical properties in connection with photochemical and biochemical aspects.[12−18,26,27] We report here the syntheses and structural characterization of *trans*-(NO, OR), *cis*-(Cl, OR)-$[RuCl(OR)(NO)(terpy)]^+$ (R = CH_3, C_2H_5, or C_3H_7) and the syntheses of isomers of $[RuCl_2(NO)(terpy)]^+$ and new nitrosyl complexes using

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alkoxonitrosylruthenium complexes as the starting complexes, as well as their spectroscopic, electrochemical, and crystal structural characterization.

Experimental Section

Measurements. IR spectra were recorded on a Perkin-Elmer FT-2000 FTIR spectrophotometer. Two kinds of samples for measurements were prepared, i.e., KBr disks and CH_3CN solutions. Elemental analyses were performed by the Sophia University Analytical Facility. ^1H and ^{13}C NMR spectra were obtained on a JEOL JML-LA500 spectrometer. UV−vis spectra were obtained on a Shimadzu MultiSpec-1500 diode-array spectrophotometer. Cyclic voltammetric measurements were made on CH_3CN or DMSO solutions containing 0.1 mol dm^{-3} tetraethylammonium perchlorate (TEAP, Nakarai Tesque Ltd.) as the supporting electrolyte with a platinum disk working electrode ($\phi = 1.6$ mm) and a Ag|0.01 mol dm^{-3} $AgNO_3$ reference electrode using a BAS 100B/W electrochemical analyzer. At the end of each measurement, ferrocene [0.07 V in CH_3CN(TEAP) vs Ag|0.01 mol dm^{-3} $AgNO_3$ (CH_3CN)] was added as an internal standard to correct redox potentials.

Materials. $K_2[RuCl_5(NO)]$ was prepared according to the methods in the literature.[28] All other solvents and chemicals were of reagent quality and were used without further purification.

Synthesis of *trans*-(Cl, Cl), *cis*-(NO, Cl)-[$RuCl_2$(NO)(terpy)]-PF_6 ([1]PF_6). This complex was synthesized by a modified method in the literature.[25] $K_2[RuCl_5(NO)]$ (400 mg, 1.03 mmol), terpy (240 mg, 1.03 mmol), and KCl (1 g, 13.4 mmol) were suspended in $C_2H_5OH-H_2O$ (3:1 v/v; 80 cm^3). The mixture was refluxed for 1 h. The resultant reddish-brown solution was cooled to room temperature, and NH_4PF_6 (350 mg; 2.15 mmol) was added. The pale-brown product obtained was collected by filtration; washed with cold water, methanol, and ether; and dried in vacuo. Yield: 320 mg (54%). This complex has been characterized in the literature.[25] ν(NO): 1895 (KBr), 1903 cm^{-1} (in CH_3CN). $E_{1/2}$, −0.48; E_{pc}, −1.01 V in CH_3CN (TEAP) vs Ag|0.01 mol dm^{-3} $AgNO_3$ (CH_3CN).

Synthesis of *trans*-(NO, OCH_3), *cis*-(Cl, OCH_3)-[RuCl(OCH_3)-(NO)(terpy)]PF_6 ([2]PF_6). This complex was synthesized previously by the reaction of [**1**]PF_6 with $NaNO_2$ in CH_3OH and characterized.[25] Here, an alternative synthetic procedure is described. [**1**]PF_6 (100 mg, 0.17 mmol) and $NaOCH_3$ (14 mg, 0.26 mmol) were suspended in dry CH_3OH (40 cm^3). The mixture was refluxed for 30 min to give a brown solution. This solution was cooled to room temperature, and NH_4PF_6 (100 mg, 0.61 mmol) was added. The solution was concentrated to ca. 3 cm^3 using a rotary evaporator. The brown product obtained was collected by filtration; washed with cold water, ethanol, and ether; and dried in vacuo. Yield: 75 mg (77%). ν(NO): 1870 (KBr), 1862 cm^{-1} (in CH_3CN). $E_{1/2}$, −0.88; E_{pc}, −1.11 V in CH_3CN(TEAP) vs Ag|0.01 mol dm^{-3} $AgNO_3$ (CH_3CN). ^1H NMR (500 MHz, CD_3CN): δ 9.12 (d, 2H, terpy-H6 and -H6″), 8.51−8.60 (m, 5H, terpy-H3, -H3′, -H3″, -H4′, and -H5′), 8.42 (t, 2H, terpy-H4 and -H4″), 7.91 (t, 2H, terpy-H5 and -H5″), 3.43 (s, 3H, $-CH_3$). ^{13}C NMR (CD_3CN): δ 157.79, 154.47, 153.10, 144.20, 143.06, 129.69, 126.54, 125.57, 58.21. ^1H NMR (DMSO-d_6): δ 9.05 (d, 2H, terpy-H6 and -H6″), 8.85−8.87 (m, 4H, terpy-H3, -H3′, -H3″, and -H5′), 8.72 (t, 1H, terpy-H4′), 8.55 (t, 2H, terpy-H4 and -H4″), 8.02 (t, 2H, terpy-H5 and -H5″), 3.34 (s, 3H, $-CH_3$). ^{13}C NMR (DMSO-d_6): δ 157.40, 153.75, 152.28, 143,95, 142.87, 129.34, 126.39, 125.37, 57.98.

Synthesis of *trans*-(NO, OC_2H_5), *cis*-(Cl, OC_2H_5)-[RuCl-(OC_2H_5)(NO)(terpy)]PF_6 ([3]PF_6). This complex was obtained by a similar procedure to [**2**]PF_6, using dry C_2H_5OH (40 cm^3) instead of dry CH_3OH. Yield: 65 mg (64%). Anal. Found: C, 34.63; H, 2.61; N, 9.47. Calcd for $C_{17}H_{16}N_4O_2ClPF_6Ru$: C, 34.62; H, 2.73; N, 9.50%. FAB-MS (*m*/*z*): 445 (M − PF_6), 410 (M − PF_6 − Cl). ν(NO): 1854 (KBr), 1860 cm^{-1} (in CH_3CN). $E_{1/2}$, −0.90; E_{pc}, −1.14 V in CH_3CN(TEAP) vs Ag|0.01 mol dm^{-3} $AgNO_3$ (CH_3CN). ^1H NMR δ(CD_3CN): 9.11 (d, 2H, terpy-H6 and -H6″), 8.51−8.61 (m, 5H, terpy-H3, -H3′, -H3″, -H4′ and -H5′), 8.42 (t, 2H, terpy-H4 and -H4″), 7.91 (t, 2H, terpy-H5 and -H5″), 3.78 (q, 2H, $-CH_{2-}$), 0.48 (t, 3H, CH_3). ^{13}C NMR (CD_3CN): δ 157.81, 154.42, 152.95, 144.09, 142.95, 129.57, 126.35, 125.44, 65.71, 19.13. ^1H NMR (DMSO-d_6): δ 9.05 (d, 2H, terpy-H6 and -H6″), 8.88−8.90 (m, 4H, terpy-H3, -H3′, -H3″, and -H5′), 8.76 (t, 1H, H4′), 8.56 (t, 2H, terpy-H4 and -H4″), 8.04 (t, 2H, terpy-H5 and -H5″), 3.75 (q, 2H, $-CH_{2-}$), 0.43 (t, 3H, CH_3). ^{13}C NMR (DMSO-d_6): δ 157.37, 153.66, 152.11, 143.81, 142.72, 129.23, 126.17, 125.19, 64.94, 19.44.

Synthesis of [RuCl(OC_3H_7)(NO)(terpy)]PF_6 ([4]PF_6). This complex was obtained by a procedure similar to that used for [**2**]-PF_6, using dry C_3H_7OH (40 cm^3) instead of dry CH_3OH. Yield: 58 mg (56%). Anal. Found: C, 35.67; H, 2.71; N, 9.12. Calcd for $C_{18}H_{18}N_4O_2ClPF_6Ru$: C, 35.80; H, 3.00; N, 9.28%. FAB-MS (*m*/*z*): 459 (M − PF_6), 400 (M − PF_6 − OC − H_7). ν(NO): 1870 (KBr), 1859 cm^{-1} (in CH_3CN). $E_{1/2}$, −0.90; E_{pc}, −1.16 V in CH_3CN(TEAP) vs Ag|0.01 mol dm^{-3} $AgNO_3$ (CH_3CN). ^1H NMR (CD_3CN): δ 9.12 (d, 2H, terpy-H6 and -H6″), 8.51−8.60 (m, 5H, terpy-H3, -H3′, -H3″, -H4′, and -H5′), 8.42 (t, 2H, terpy-H4 and -H4″), 7.91(t, 2H, terpy-H5 and -H5″), 3.71 (q, 2H, $-OCH_{2-}$), 0.82 (m, 2H, $-CH_{2-}$), 0.23 (t, 3H, CH_3). ^1H NMR (DMSO-d_6): δ 9.07 (d, 2H, terpy-H6 and -H6″), 8.93−8.91 (m, 4H, terpy-H3, -H3′, -H3″, and -H5′), 8.78 (t, 1H, H4′), 8.58 (t, 2H, terpy-H4 and -H4″), 8.05 (t, 2H, terpy-H5 and -H5″), 3.67 (q, 2H, $-OCH_{2-}$), 0.78 (m, 2H, $-CH_{2-}$), 0.18 (t, 3H, CH_3).

Reaction of [3]PF_6 with Hydrochloric Acid To Give *trans*-(NO, Cl), *cis*-(Cl, Cl)-[$RuCl_2$(NO)(terpy)]PF_6 ([5]PF_6). [**3**]PF_6 (50 mg, 0.085 mmol) was suspended in hydrochloric acid (12 mol dm^{-3}, 10 cm^3). The mixture was stirred for 5 h and warmed to about 40 °C. A brown solution was obtained, and NH_4PF_6 (600 mg, 3.68 mmol) was added. The light-brown product obtained was collected by filtration; washed with cold water, ethanol, and ether; and dried in vacuo. Yield: 26 mg (53%). Anal. Found: C, 31.34; H, 1.95; N, 9.52. Calcd for $C_{15}H_{11}N_4OClPF_6Ru$: C, 31.05; H, 1.91; N, 9.66%. FAB-MS (*m*/*z*): 435 (M − PF_6), 400 (M − PF_6 − Cl), 365 (M − PF_6 − 2Cl), 335 (M − PF_6 − 2Cl − NO). ν(NO): 1928 (KBr), 1904 cm^{-1} (in CH_3CN). $E_{1/2}$, −0.43; E_{pc}, −0.78 V in CH_3CN(TEAP) vs Ag|0.01 mol dm^{-3} $AgNO_3$ (CH_3CN). ^1H NMR (CD_3CN): δ 9.17 (d, 2H, terpy-H6 and -H6″), 8.57−8.65 (m, 5H, terpy-H3, -H3′, -H3″, -H4′ and -H5′), 8.45 (t, 2H, terpy-H4 and -H4″), 7.95 (t, 2H, terpy-H5 and -H5″). ^{13}C NMR (CD_3CN): δ 157.84, 154.29, 153.66, 144.76, 143.36, 129.99, 126.94, 125.93. ^1H NMR (DMSO-d_6): δ 9.09 (d, 2H, terpy-H6 and -H6″), 8.94−8.97 (m, 4H, terpy-H3, -H3′, -H3″, and -H5′), 8.81 (t, 1H, terpy-H4′), 8.59 (t, 2H, terpy-H4 and -H4″), 8.06 (t, 2H, terpy-H5 and -H5″). ^{13}C NMR (DMSO-d_6): δ 157.58, 153.77, 152.95, 144.49, 143.06, 129.55, 126.63, 125.49.

(27) (a) Stagni, S.; Palazzi, A.; Zacchini, S.; Ballarin, B.; Bruno, C.; Marcaccio, M.; Paolucci, F.; Monari, M.; Carano, M.; Bard, A. J. *Inorg. Chem.* **2006**, *45*, 695. (b) Rachford, A. A.; Petersen, J. L.; Rack, J. J. *Inorg. Chem.* **2005**, *44*, 8065. (c) Sharma, S.; Singh, S. K.; Chandra, M.; Pandey, D. S. *J. Inorg. Biochem.* **2005**, *99*, 458. (d) Fabre, M. A.; Jaud, J.; Bonvoisin, J. J. *Inorg. Chim. Acta* **2005**, *358*, 2384. (e) Bonnet, S.; Collin, J.-P.; Gruber, N.; Sauvage, J.-P. Schofield, E. R. *J. Chem. Soc., Dalton Trans.* **2003**, 4654.

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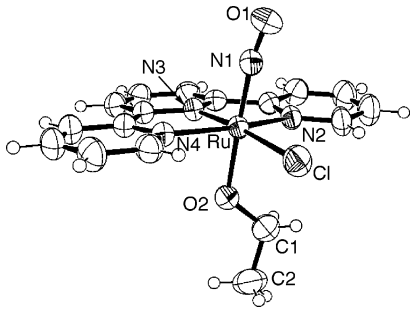

Figure 1. Structure of *trans*-(NO, OC_2H_5), *cis*-(Cl, OC_2H_5)-[RuCl(OC_2H_5)(NO)(terpy)]$^+$ ([**3**]$^+$).

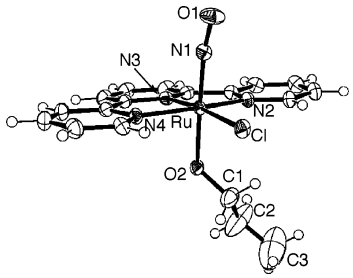

Figure 2. Structure of *trans*-(NO, OC_3H_7), *cis*-(Cl, OC_3H_7)-[RuCl(OC_3H_7)(NO)(terpy)]$^+$ ([**4**]$^+$).

[**5**]PF_6 was also obtained by reactions of [**2**]PF_6 and [**4**]PF_6 as the starting complex instead of [**3**]PF_6 under the same conditions.

Reaction of [3]PF_6 with HSO_3CF_3 in CH_3CN To Give *trans*-(NO, Cl), *cis*-(CH_3CN, Cl)-[RuCl(NO)(CH_3CN)(terpy)]$(PF_6)_2$ ([6]$(PF_6)_2$). [**3**]PF_6 (28 mg, 0.047 mmol) was dissolved in CH_3CN (10 cm^3), and 11 M HSO_3CF_3 (25 μL) was added. The mixture was refluxed for 5 h. The solution was concentrated to ca. 5 cm^3 using a rotary evaporator. NH_4PF_6 (100 mg, 0.61 mmol) was added as a precipitant. The yellow solution was allowed to stand under an ether atmosphere, and then yellow crystals appeared. The yellow crystals were collected and washed with ether. Yield: 12 mg (35%). The volume of the filtrate was reduced to give a mixture of PF_6 and CF_3SO_3 salts of [**6**]$^{2+}$. Anal. Found: C, 27.40; H, 1.91; N, 9.60. Calcd for $C_{17}H_{14}N_5OClP_2F_{12}Ru$: C, 27.94; H, 1.93; N, 9.58%. ν(NO): 1951 (KBr), 1935 cm^{-1} (in CH_3CN). $E_{1/2}$, -0.08; E_{pc}, -0.69 V in CH_3CN(TEAP) vs Ag|0.01 mol dm^{-3} $AgNO_3$ (CH_3CN). ^{1}H NMR (CD_3CN): δ 8.99 (d, 2H, terpy-H6 and -H6″), 8.69 (t, 1H, terpy-H4′), 8.56−8.64 (m, 4H, terpy-H3, -H3′, -H3″, and -H5′), 8.52 (t, 2H, terpy-H4 and -H4″), 8.00 (t, 2H, terpy-H5 and -H5″), 2.82 (s, 3H, −CH−). ^{13}C NMR (CD_3CN): δ 157.70, 155.26, 155.16, 146.18, 144.71, 130.87, 128.01, 126.99, 5.35.

Similar reactions of [**2**]PF_6 and [**4**]PF_6 with HSO_3CF_3 in CH_3CN were carried out, giving the same complex, *trans*-(NO, Cl), *cis*-(CH_3CN, Cl)-[RuCl(NO)(CH_3CN)(terpy)]$(PF_6)_2$ {[**6**]$(PF_6)_2$} in equivalent yields.

Reaction of [1]PF_6 in H_2O in the Presence of KCl. [**1**]PF_6 (50 mg, 0.085 mmol) was suspended in H_2O (10 cm^3) in the presence of KCl (50 mg, 0.67 mmol). The mixture was refluxed for 5 h and cooled to room temperature. NH_4PF_6 (70 mg, 0.43 mmol) was added as a precipitant. The yellow product obtained was collected by filtration; washed with cold water, methanol, and ether; and dried in vacuo (16 mg). This product showed a broad ν(NO) band at around 1900 and a weak band at 1855 cm^{-1}. The complexes showing the broad ν(NO) band were confirmed to be a 1:1 mixture of [**1**]PF_6 and [**5**]PF_6 by CV and ^{1}H NMR spectroscopy. The filtrate of the above procedure was allowed to stand for a few days, and its volume was reduced by slow evaporation to give yellow crystals (8 mg). This yellow complex was identified as *trans*-(NO, OH), *cis*-(Cl, OH)-[RuCl(OH)(NO)(terpy)]PF_6, whose structure was previously determined in the literature.[16] Anal. Found: C, 31.97; H, 1.90; N, 9.95. Calcd for $C_{15}H_{12}N_4O_2ClPF_6Ru$: C, 32.07; H, 2.15; N, 9.97%. ν(NO), 1855 cm^{-1} (KBr). From the remaining solution, a mixture of [**1**]PF_6, [**5**]PF_6, and *trans*-(NO, OH), *cis*-(Cl, OH)-[RuCl(OH)(NO)(terpy)]PF_6 was obtained by evaporation (16 mg).

Reaction of [1]PF_6 in H_2O in the Presence of Hydrochloric Acid. [**1**]PF_6 (50 mg, 0.085 mmol) was suspended in H_2O (10 cm^3) in the presence of hydrochloric acid (37%, 400 μL; 5.00 mmol). The mixture was refluxed for 5 h and cooled to room temperature. NH_4PF_6 (70 mg, 0.43 mmol) was added as a precipitant. The yellow product obtained was collected by filtration; washed with cold water, methanol, and ether; and dried in vacuo (41 mg). This product was confirmed to be a 1:1 mixture of [**1**]PF_6 and [**5**]PF_6 by CV and IR and ^{1}H NMR spectroscopies. From the filtrate, a mixture of [**1**]PF_6, [**5**]PF_6, and a few nitrosyl complexes was obtained by evaporation (7 mg).

Reaction of [1]PF_6 with $NaOCH_3$. The reaction of [**1**]PF_6 in a CH_3CN solution with $NaOCH_3$ that was dissolved in a small amount of CH_3OH was monitored by UV−vis and IR spectroscopies. [**1**]-PF_6 (8.00×10^{-5} mol dm^{-3}, 3.5 cm^3) was dissolved in dry CH_3CN, and an equimolar amount of $NaOCH_3$ dissolved in dry CH_3OH (8.00×10^{-3} mol dm^{-3}, 35 μL) was added. UV−vis spectra of the reaction mixture were measured as shown in Figure S10 (Supporting Information). [**1**]PF_6 (31 mg, 0.053 mmol) was dissolved in dry CH_3CN (7 cm^3), and an IR spectrum was recorded. A methanol solution of $NaOCH_3$ (8.00×10^{-3} mol dm^{-3}, 950 μL) was added to the CH_3CN solution of [**1**]PF_6. The solution color changed immediately from brown to dark purple. An IR spectrum of the resulting solution was recorded as shown in Figure S11.

X-ray Crystallography. Single crystals of *trans*-(NO, OC_2H_5), *cis*-(Cl, OC_2H_5)-[RuCl(OC_2H_5)(NO)(terpy)]PF_6 ([**3**]PF_6) were obtained by recrystallization from a CH_3CN solution containing small amounts of ethanol and water and then vapor diffusion of ether into the solution. Single crystals of *trans*-(NO, OC_3H_7), *cis*-(Cl, OC_3H_7)-[RuCl(OC_3H_7)(NO)(terpy)]PF_6·CH_3CN ([**4**]PF_6·CH_3CN) were obtained by recrystallization from a CH_3CN solution and then vapor diffusion of ether into the solution. Single crystals of *trans*-(NO, Cl), *cis*-(Cl, Cl)-[$RuCl_2$(NO)(terpy)]CF_3SO_3 ([**5**]CF_3SO_3) were obtained by recrystallization from a CH_3CN/H_2O solution containing $NaSO_3CF_3$ and then vapor diffusion of ether into the solution. Single crystals of *trans*-(NO, Cl), *cis*-(CH_3CN, Cl)-[RuCl(NO)(CH_3CN)-(terpy)]$(PF_6)_2$ {[**6**]$(PF_6)_2$} were obtained from a CH_3CN solution by vapor diffusion of ether. The intensity data were collected on a Rigaku Mercury CCD diffractometer, using graphite-monochromatized Mo Kα radiation (0.71069 Å). All calculations were performed using the Crystal Structure software package.[29] Structures were solved by direct methods, expanded using Fourier techniques, and refined using full-matrix least-squares techniques. The crystallographic data are summarized in Table 1.

Results

Synthesis and Characterization of Alkoxo Complexes. *trans*-(NO, OCH_3), *cis*-(Cl, OCH_3)-[RuCl(OCH_3)(NO)(terpy)]-PF_6 ([**2**]PF_6) was synthesized by the reaction of *trans*-(Cl, Cl), *cis*-(NO, Cl)-[$RuCl_2$(NO)(terpy)]$^+$ ([**1**]$^+$) with $NaOCH_3$ in CH_3OH. [**2**]PF_6 had previously been synthesized by the reaction of the same starting complex with $NaNO_2$ in CH_3-OH and characterized.[25] The present procedure gave [**2**]$^+$ in

(29) *Crystal Structure 3.6.0, Single Crystal Structure Analysis Software*; Molecular Structure Corp. and Rigaku Corp.: The Woodlands, TX, and Tokyo, Japan, 2004.

Table 1. Crystallographic Data for [**3**]PF_6, [**4**]PF_6·CH_3CN, [**5**]CF_3SO_3, and [**6**]$(PF_6)_2$

	[**3**]PF_6	[**4**]PF_6·CH_3CN	[**5**]CF_3SO_3	[**6**]$(PF_6)_2$
formula	$C_{17}H_{16}O_2N_4F_6PClRu$	$C_{20}H_{21}O_2N_5ClF_6PRu$	$C_{16}H_{11}O_4N_4F_3SCl_2Ru$	$C_{17}H_{14}ON_5F_{12}P_2ClRu$
fw	589.83	644.91	584.32	730.78
color of crystal	orange	orange	yellow	yellow
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_12_12_1$	$P2_1/n$
a (Å)	8.7534(4)	10.600(2)	8.0868(5)	12.439(3)
b (Å)	8.5519(5)	17.042(3)	9.2038(5)	12.048(3)
c (Å)	28.833(2)	13.817(3)	27.511(2)	17.201(4)
β (deg)	93.5582(7)	106.2300(9)		91.0075(9)
V (Å^3)	2154.2(2)	2396.5(8)	2047.6(2)	2577.3(10)
Z	4	4	4	4
D_{calcd} (g cm^{-3})	1.818	1.787	1.895	1.883
μ(Mo Kα) (cm^{-1})	10.00	9.08	11.88	9.45
T (°C)	25	−150	25	25
R^a	0.0420	0.0372	0.0430	0.0522
$R_w{}^b$	0.1380	0.1033	0.1160	0.1735
GOF	1.006	1.005	1.012	0.974

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$ [$I > 2\sigma(I)$]. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ (all reflections).

Table 2. Data of ν(NO), Reduction Potentials, and UV−Vis Absorption Spectra

complex	ν(NO) (cm^{-1}) solid[a]	ν(NO) (cm^{-1}) solution[b]	$E_{1/2}{}^c$ (V)	$E_{pc}{}^c$ (V)	λ (nm) ($10^{-4}\epsilon$ (M^{-1} cm^{-1}))
[**1**]PF_6	1895	1903	−0.48	−1.01	296 sh (0.99), 352 (1.13), 381 sh (0.33), 477 (0.02)
[**2**]PF_6	1870	1862	−0.88	−1.11	275 (1.79), 337 (1.25), 404 (0.08)
[**3**]PF_6	1854	1860	−0.90	−1.14	273 (1.47), 336 (1.06), 416 (0.09)
[**4**]PF_6	1870	1859	−0.90	−1.16	275 (1.47), 336 (1.06), 415 (0.08)
[**5**]PF_6	1928	1904	−0.43	−0.78	279 (1.72), 342 (1.10), 474 (0.05)
[**6**]$(PF_6)_2$	1951	1935	−0.08	−0.69	273 (1.64), 312 (0.93), 356 (0.92), 521 (0.04)
[Ru(NO_2)(OH)(NO)(terpy)]$PF_6{}^d$	1860		−0.79	−1.22	
[RuCl(OH)(NO)(terpy)]$PF_6{}^e$	1855		−0.95[f]	−1.16	

[a] KBr disk. [b] In CH_3CN. [c] V vs Ag|0.01 M $AgNO_3$. [d] *trans*-(NO, OH), *cis*-(NO_2, OH) form, ref 25. [e] *trans*-(NO, OH), *cis*-(Cl, OH) form, refs 14 and 16. The redox potentials were measured in DMSO because the complex is insoluble in CH_3CN. [f] The value is E_{pc} because the wave is irreversible.

a higher yield, over 70%, than the previous method, and reactions were carried out in C_2H_5OH and C_3H_7OH instead of CH_3OH under the same conditions to form the corresponding ethoxo and propoxo complexes, *trans*-(NO, OC_2H_5), *cis*-(Cl, OC_2H_5)-[RuCl(OC_2H_5)(NO)(terpy)]PF_6 ([**3**]PF_6) and *trans*-(NO, OC_3H_7), *cis*-(Cl, OC_3H_7)-[RuCl(OC_3H_7)(NO)-(terpy)]PF_6 ([**4**]PF_6), respectively, which were characterized by IR and NMR spectroscopies, CV, and X-ray crystallography (Figures 1 and 2). The reaction of [**1**]PF_6 in CH_3OH, C_2H_5OH, or C_3H_7OH does not proceed without $NaOCH_3$ under refluxing conditions. The reaction of [**1**]PF_6 with $NaOCH_3$ was carried out in CH_3CN, instead of CH_3OH, and monitored by UV−vis and IR spectroscopies. The color of the acetonitrile solution of [**1**]PF_6 immediately changed from brown to dark purple upon addition of a methanolic solution of $NaOCH_3$. The intensity of the UV−vis band at 352 nm assigned to [**1**]$^+$ decreased, and new bands appeared at 320 and 485 nm and increased in intensity (Figure S10). The intensity of the strong ν(NO) band at 1903 cm^{-1} in CH_3CN decreased upon addition of a methanol solution of $NaOCH_3$ (Figure S11).

Characteristic data of the synthesized and related complexes are reported in Table 2. The IR spectra of the alkoxo complexes [**2**]PF_6, [**3**]PF_6, and [**4**]PF_6 obtained show a strong NO stretching vibration at 1870, 1854, and 1870 cm^{-1}, respectively, on samples prepared as KBr disks and at 1862, 1860, and 1859 cm^{-1}, respectively, in CH_3CN solutions. In ^{1}H NMR spectra in CD_3CN, protons of the terpy ligand of the alkoxo complexes are observed in the range 9.12−7.91 ppm, and those of the methoxo, ethoxo, and propoxo ligands, $-CH_3$, $-CH_2-$, and OCH_2-, are observed at 3.43 ppm for [**2**]PF_6; 0.48 and 3.75 ppm for [**3**]PF_6; and 0.23, 0.82, and 3.71 ppm for [**4**]PF_6 (Figure S1). Cyclic voltammograms of alkoxo complexes in CH_3CN containing TEAP reveal reversible and irreversible one-electron reduction waves at −0.88 and −1.11 V −for [**2**]PF_6, −0.90 and −1.14 V for [**3**]PF_6, and −0.90 and −1.16 V for [**4**]PF_6 (Figure S6). The first reversible waves of these three complexes were confirmed as Nernstian waves by CV and normal pulse voltammetry (NPV) and were observed in the negative region compared to those of similar nitrosylruthenium complexes having polypyridyl ligand(s) such as *cis*-[RuCl(NO)(bpy)$_2$]-$(PF_6)_2$ [−0.12 V in CH_3CN vs Ag|0.01 mol dm^{-3} $AgNO_3$ (CH_3CN)].[30] The structures of [**3**]PF_6 and [**4**]PF_6 were determined by X-ray crystallography to be similar to that of [**2**]PF_6, which had been reported previously.[25] The nitrosyl ligand of these alkoxo complexes moves from the equatorial position of the terpy plane in the starting complex to an axial position. In the electronic spectra of alkoxonitrosyl complexes in acetonitrile solution (Figure S9), the intense bands around 270 and 335 nm are similar to the $\pi-\pi^*$(terpy) and dπ(Ru)−π^*(terpy) transitions, respectively, that have been reported for typical terpyridine complexes.[12,15,17] These nitrosyl comlexes show a weak band around 420 nm that is assigned to the d−d transition overlapped with a dπ(Ru)−π^*(NO) transition.[21a,31]

(30) Callahan, R. W.; Meyer, T. J. *Inorg. Chem.* **1977**, *16*, 574.

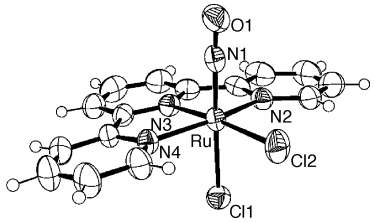

Figure 3. Structure of *trans*-(NO, Cl), *cis*-(Cl, Cl)-$[RuCl_2(NO)(terpy)]^+$ ($[\mathbf{5}]^+$).

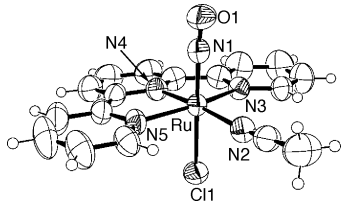

Figure 4. Structure of *trans*-(NO, Cl), *cis*-(CH_3CN, Cl)-$[RuCl(NCCH_3)(NO)(terpy)]^{2+}$ ($[\mathbf{6}]^{2+}$).

Reactions of Alkoxo Complexes. The alkoxo ligand (RO^-) locates at the trans position with respect to the nitrosyl ligand and reacts with a proton to afford an alcohol complex [Ru−O(H)R], whose alcohol ligand is easily substituted by another ligand. *trans*-(NO, OR), *cis*-(Cl, OR)-$[RuCl(OR)(NO)(terpy)]^+$ complexes can be used as a precursor for the synthesis of new *trans*-(NO, X), *cis*-(Cl, X)-type nitrosyl complexes. Alkoxo complexes are stable in solvents such as CH_3CN, CH_3NO_2, and alcohol at room temperature for at least 1 week. An ethanol solution of the methoxo complex, $[\mathbf{2}]PF_6$, was refluxed for 6 h, and the resultant solution was evaporated to dryness to give the ethoxo complex, which was confirmed by $-CH_3$ and $-CH_2-$ proton signals in the ^1H NMR spectrum in CD_3CN (Figure S4a). On the other hand, the ^1H NMR spectrum in CD_3CN of a solid isolated from the reaction mixture of the ethoxo complex, $[\mathbf{3}]PF_6$, in methanol indicated that this solid is a mixture of methoxo and ethoxo complexes in a ratio of 1:4 as determined by integration of the $-CH_3$ signals (Figure S4b). Thus, the methoxo complex is changed to the ethoxo complex in ethanol by refluxing for 6 h, and the ethoxo complex, $[\mathbf{3}]^+$, is stable in methanol under refluxing conditions.

Although the $[RuCl(OR)(NO)(terpy)]^+$ complexes did not react with CF_3SO_3H in CH_3NO_2 under stirring conditions, a reaction of $[\mathbf{3}]PF_6$ with hydrochloric acid solution under refluxing conditions gave a new nitrosyl complex having a strong ν(NO) band at 1928 cm^{-1} and characteristic nitrosyl ligand reduction waves by CV in CH_3CN at −0.43 and −0.78 V (Figure S5). The alkoxo ligand was substituted by the chloro ligand to give $[RuCl_2(NO)(terpy)]^+$, $[\mathbf{5}]^+$, which is a geometric isomer of $[\mathbf{1}]^+$. The structure of $[\mathbf{5}]^+$ as the CF_3SO_3 salt was determined by X-ray crystallography and found to have a *trans*-(NO, Cl), *cis*-(Cl, Cl) configuration (Figure 3).

The reaction of $[3]PF_6$ with CF_3SO_3H in acetonitrile solution afforded a solvated complex, $[RuCl(NO)(NCCH_3)(terpy)]^{2+}$ ($[\mathbf{6}]^{2+}$), in which the chloro ligand moved from a cis position with respect to the nitrosyl ligand to a trans position. This complex shows the ν(NO) band at 1951 cm^{-1} and reversible and irreversible reduction waves by CV in CH_3CN at −0.08 and −0.69 V (Figure S5), respectively. The structure of $[\mathbf{6}](PF_6)_2$ was determined by X-ray crystallography and is shown in Figure 4.

Structural Characterization. Selected structural parameters of $[\mathbf{3}]PF_6$, $[\mathbf{4}]PF_6$, $[\mathbf{5}]CF_3SO_3$, $[\mathbf{6}](PF_6)_2$, and the related complexes $[\mathbf{1}]PF_6$ and $[\mathbf{2}]PF_6$ are summarized in Table 3. The bond distances, Ru−N(nitrosyl) (1.737−1.780 Å) and N−O (1.109−1.154 Å), and the angles, Ru−N−O (171.3−176.3°), of these complexes are similar to those of reported $\{RuNO\}^6$-type nitrosylrutheium complexes containing the terpy ligand, indicating that these complexes can be classified as $\{RuNO\}^6$-type complex.[14−16,18] The distances between the ruthenium and nitrogen atoms of the terpy ligand are characteristic; those of the terminal nitrogen atoms (2.081−2.096 Å) are longer than that of the central one (1.984−1.989 Å). The Ru−O distances of the Ru−OEt moiety in $[\mathbf{3}]PF_6$ (1.943 Å) and the Ru−OPr moiety in $[\mathbf{4}]PF_6$ (1.958 Å) are similar to that of the Ru−OMe moiety in $[\mathbf{2}]PF_6$. There is a definite difference in the Ru−Cl bond distance between cis and trans positions with respect to the NO ligand. The distances of the chloro ligand at a cis position (2.399 Å for $[\mathbf{3}]PF_6$, 2.396 Å for $[\mathbf{4}]PF_6$, and 2.385 Å for $[\mathbf{5}]CF_3SO_3$) are greater than those at a trans position {2.341 Å for $[\mathbf{5}]CF_3SO_3$ and 2.319 Å for $[\mathbf{6}](PF_6)_2$}.

Stability and Reactivity of *trans*-(Cl, Cl), *cis*-(NO, Cl)-$[RuCl_2(NO)(terpy)]^+$ ($[\mathbf{1}]^+$). $[\mathbf{1}]PF_6$ was synthesized by the reaction of $K_2[RuCl_5(NO)]$ with terpy in H_2O/ethanol (1:3; v/v) in the presence of KCl under refluxing for 1 h. To isolate all products of this reaction, the reaction mixture was concentrated to dryness and recrystallized from CH_3CN to remove insoluble inorganic materials such as KCl without addition of NH_4PF_6. A cyclic voltammogram of the mixture of complexes obtained as Cl salts in DMSO containing 0.1 mol dm^{-3} TEAP showed three reduction waves, assignable to reductions of $[\mathbf{1}]^+$ and $[\mathbf{5}]^+$ (Figure S8a). This mixture was dissolved in H_2O, and then the NH_4PF_6 was added as a precipitant to the solution after it had been filtered to remove an insoluble complex, affording a mixture obtained as PF_6 salts. A cyclic voltammogram of the mixture in CH_3CN containing 0.1 mol dm^{-3} TEAP revealed that this mixture consisted at least of three complexes, $[\mathbf{1}]PF_6$, $[Ru(terpy)_2](PF_6)_2$, and *trans*-(NO, Cl), *cis*-(Cl, Cl)-$[RuCl_2(NO)(terpy)]PF_6$ ($[\mathbf{5}]PF_6$), the latter of which is a geometrical isomer of $[\mathbf{1}]^+$ (Figure S8b). It is clear that $[\mathbf{1}]^+$ was a main product and $[\mathbf{5}]^+$ was a minor product, as determined by comparison of the wave heights of the reduction waves for $[\mathbf{1}]^+$ and $[\mathbf{5}]^+$.

No UV−vis spectral change of $[\mathbf{1}]PF_6$ was observed in organic solvents such as CH_3CN, $(CH_3)_2CO$, CH_3OH, and C_2H_5OH for at least 4 days, although the spectrum in H_2O changed in a few days. Thus, $[\mathbf{1}]^+$ is stable in these organic solvents at room temperature. Reactions of $[\mathbf{1}]PF_6$ in aqueous KCl or HCl solutions were carried out for 3 h, and a solid product was obtained by addition of NH_4PF_6 to the resultant solution. The results of the IR spectral measurements of the solid and cyclic voltammograms in CH_3CN indicate the

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Table 3. Selected Bond Distances (Å) and Angles (deg)

	[**3**]PF_6	[**4**]PF_6	[**5**]CF_3SO_3	[**6**]$(PF_6)_2$	[**1**]PF_6[a]	[**2**]PF_6[a]
N−O(nitrosyl)	1.154(5)	1.145(2)	1.142(7)	1.109(5)	1.129(4)	1.129(5)
Ru−N(nitrosyl)	1.756(3)	1.766(2)	1.737(5)	1.780(4)	1.765(7)	1.753(4)
Ru−N(terminal trpy)	2.093(3)	2.094(2)	2.088(4)	2.081(3)	2.083(3)	2.087(4)
	2.096(3)	2.081(2)	2.090(4)	2.085(3)	2.073(3)	2.075(4)
Ru−N(central trpy)	1.989(3)	1.988(2)	1.999(4)	1.984(3)	2.015(3)	1.982(4)
Ru−L						
trans with	L = OEt	L = OPr	L = Cl	L = Cl		L = OMe
respect to NO	1.943(3)	1.958(2)	2.341(2)	2.319(1)		1.940(3)
cis with	L = Cl	L = Cl	L = Cl	L = CH_3CN	L = Cl	L = Cl
respect to NO	2.399(1)	2.396(1)	2.385(2)	2.086(3)	2.357(1)	2.387(1)
					2.375(1)	
Ru−N−O(nitrosyl)	171.0(3)	170.8(2)	176.3(4)	175.6(3)	174.6(3)	168.3(4)
N(terminal trpy)−Ru −N(terminal trpy)	159.4(1)	159.7(1)	159.4(2)	159.2(1)	157.4(1)	159.8(1)
N(central trpy)−Ru	79.6(1)	80.2(1)	79.9(2)	79.9(1)	78.6(1)	80.0(1)
−N(terminal trpy)	79.9(1)	79.7(1)	80.0(2)	79.9(1)	78.9(1)	80.0(1)

[a] Reference 25.

formation of two isomers of $[RuCl_2(NO)(terpy)]^+$, $[\mathbf{1}]^+$ and $[\mathbf{5}]^+$. They exhibit a characteristic band of the NO ligand at 1895 and 1928 cm^{-1} and show one reversible redox wave at around −0.5 V and two irreversible reduction waves at −0.8 and −1.1 V. The ESI-MS spectrum in CH_3OH shows only a peak centered at $m/z = 435$, which corresponds to $[RuCl_2(NO)(terpy)]^+$. Thus, the complex having the ν(NO) band at 1895 cm^{-1} and reduction waves at −0.5 and −1.1 V was assigned to [**1**]PF_6, and that having the ν(NO) band at 1928 cm^{-1} and reduction waves at −0.5 and −0.8 V was assigned to [**5**]PF_6 by comparison with data of complexes that were synthesized and characterized as authentic samples. The solid was a mixture consisting of nearly equal quantities of these two isomers, as confirmed by ^1H NMR spectroscopy (Figure S3). In the reaction of $[\mathbf{1}]^+$ with an aqueous HCl solution, these two isomers were the main products. In the reaction of $[\mathbf{1}]^+$ with a KCl solution, *trans*-(NO, OH), *cis*-(Cl, OH)-$[RuCl(OH)(NO)(terpy)]^+$, which showed a characteristic ν(NO) band at 1855 cm^{-1}, also formed in addition to these isomers.

Discussion

Synthesis and Geometrical Configuration of Alkoxonitrosyl Complexes. [**1**]PF_6 is easily synthesized in high yield using as a starting material $[RuCl_5(NO)]^{2-}$, which is a useful complex for the synthesis of chloronitrosylruthenium complexes and has a potential application to the synthesis of new nitrosyl complexes. Bottomley has proposed that nitrosyl complexes with ν(NO) > 1890 cm^{-1} react with at least one nucleophile.[24] In a previous work, we reported that nitrosylruthenium complexes containing pyca ligands with ν(NO) $\approx$ 1890 cm^{-1} do not react with nucleophiles at the nitrogen atom of the NO ligand.[22] The nitrosyl ligand in $[\mathbf{1}]^+$ is thus located at the boundary of being reactive and nonreactive toward nucleophiles at its nitrogen atom, according to the electrochemical and IR properties of $[\mathbf{1}]^+$. In another report on the reaction of $[\mathbf{1}]^+$ with N_3^- in CH_3CN,[25] however, we showed that the N_3^- ion attacks the nitrogen atom of the nitrosyl ligand to afford $[RuCl_2(CH_3CN)(terpy)]^+$ and $[RuCl(CH_3CN)_2(terpy)]^+$ and that reaction of $[\mathbf{1}]^+$ under basic aqueous conditions affords ruthenium complexes containing no NO ligand. It can thus be concluded that the nitrosyl ligand in $[\mathbf{1}]^+$ shows electrophilicity and belongs to the group of nitrosyl complexes that are reactive toward nucleophiles. Although this dichloronitrosyl complex, $[\mathbf{1}]^+$, does not react in alcohol without a Lewis base such as nitrite and alkoxide ions under refluxing conditions, reactions with a slight excess of NO_2^- in H_2O and CH_3OH give $[Ru(NO_2)(OH)(NO)(terpy)]^+$ and $[RuCl(OCH_3)(NO)(terpy)]^+$, respectively.[25] A reaction of [**1**]PF_6 with $NaOCH_3$ in CH_3CN occurs to give a dark purple solution. The intensity of the characteristic ν(NO) IR band of [**1**]PF_6 in a CH_3CN solution decreases upon addition of $NaOCH_3$ (Figure S11). This reaction is an alternative to the formation of the methoxonitrosyl complex [**2**]PF_6 and occurs through the nucleophilic attack of CH_3O^- on the nitrosyl nitrogen in a manner similar to the reaction of $[RuCl(NO)(bpy)_2]^{2+}$ with CH_3O^-, affording a methyl nitrite ligand [−N(O)OCH_3] that had been reported by Meyer et al.[32] Changes in the UV−vis spectrum of [**1**]PF_6 upon addition of $NaOCH_3$ (Figure S10a) and NaN_3 (Figure S10b) reveal the formation of the same product as obtained from the reaction of [**1**]PF_6 with $NaOCH_3$ in CH_3CN, the acetonitrile complex $[RuCl(CH_3CN)_2(terpy)]^+$, which has been characterized by Walsh et al. and shows characteristic UV−vis absorption bands at 320 and 485 nm,[33] via formation of a methyl nitrite complex. On the other hand, the present synthetic reactions of [**1**]PF_6 with $NaOCH_3$ in methanol, ethanol, and propanol give methoxo-, ethoxo-, and propoxonitrosyl complexes, respectively, in high yields.[34] The methoxide ion functions mainly as a ligand entering the coordination sphere of the ruthenium center under the present reaction conditions. The alkoxo ligand of the product comes from the solvent and coordinates to the ruthenium center at the trans position with respect to the nitrosyl ligand, as it functions as an electron donor to stabilize the nitrosyl complex (Scheme 1).

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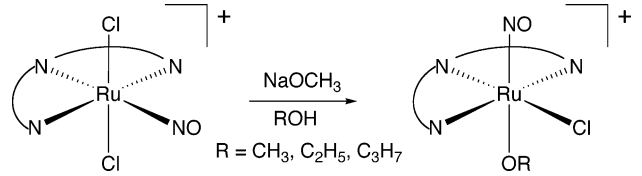
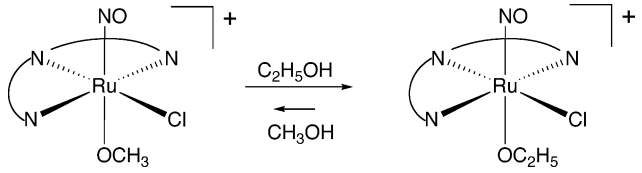
(34) After isolation of [**1**]PF_6 by filtration, [**1**]PF_6 was obtained again by slow evaporation of the filtrate. The total yield of [**1**]PF_6 was over 90%.

Scheme 1. Reaction of $[\mathbf{1}]^+$ with Alkoxide Ion in Alcohol



Scheme 2. Reactions of Alkoxo Complexes in Alcohol



In reactions of $[\mathbf{1}]PF_6$ with a Lewis base as an entering ligand, the composition and geometrical configuration of the product depend on the natures of the Lewis base and the solvent. A recent report on substitution reactions of terpy complexes by Eldik et al. shows that these substitution reactions proceed according to an associative process.[13] The reaction of $[\mathbf{1}]PF_6$ with an entering ligand such as NO_2^- or CH_3O^- in H_2O, CH_3OH, C_2H_5OH, and C_3H_7OH affords $[RuX(OR)(NO)(terpy)]^+$ (R = H, CH_3, C_2H_5, or C_3H_7; X = NO_2 or Cl), whose geometrical configuration around the Ru center is a *trans*-(NO, OR), *cis*-(X, OR) form given that the nitro ligand showing the π-acceptor character and the chloro ligand showing the weaker π-donor character than the alkoxo ligand prefer to coordinate in the cis position with respect to the nitrosyl ligand and the hydroxo and alkoxo ligands coming from water and alcohol as the solvent, respectively, coordinate in the trans position. Thus, the composition and geometrical configuration of the final product depend on the properties of the fifth, sixth, and entering ligands that come from the substrate and solvent and are explained in terms of the interaction between the NO and the coexisting ligands. The NO ligand is stabilized by coordination of a π-donor ligand at the trans position, as exemplified by the IR spectra and electrochemical properties of the alkoxo complexes. From the CV results reported in Table 2 and Figure S6, the alkoxo and hydroxo complexes exhibit negative $E_{1/2}$ values in CH_3CN solution. The IR spectra of these nitrosyl complexes show the strong ν(NO) band at around 1900 cm^{-1} as reported in Table 2. These values of ν(NO) for KBr disks of this series of nitrosyl complexes are influenced by the counteranion such as PF_6^-. The relationship between the values of ν(NO) in CH_3CN solution and the reduction potential is almost linear, similar to those of the reported nitrosyl complexes.[4,20,21,24] The reactivity and nature of the nitrosyl ligand in the terpy series complexes are better estimated from the ν(NO) value in CH_3CN solution than from the value for the KBr disk.

Reaction of Alkoxo Complexes. The methoxo ligand of $[\mathbf{2}]^+$ can be substituted by an ethoxo ligand in ethanol under refluxing conditions, whereas the reaction of $[\mathbf{3}]^+$ in methanol gives a 1:4 mixture of $[\mathbf{2}]^+$ and $[\mathbf{3}]^+$ (Figure S4, Scheme 2).

These results are explained by the differences in basicity between methoxide and ethoxide ions coordinated to the ruthenium center, the differences in acidity between methanol and ethanol, and the differences in reduction potential and ν(NO) between $[\mathbf{2}]^+$ (−0.88 V and 1862 cm^{-1}) and $[\mathbf{3}]^+$ (−0.90 V and 1860 cm^{-1}), indicating that the nitrosyl ligand of $[\mathbf{3}]^+$ is slightly more electron-attracting toward the ethoxo ligand than is that of $[\mathbf{2}]^+$.

The alkoxo ligand dissociates from the metal center into an alcohol by reaction with a proton donor such as hydrochloric acid. It is possible that the reaction of an alkoxo complex with a protic acid conjugated to an entering ligand gives a new complex whose configuration around the ruthenium center is the same as that of the starting complex. Hydrochloric acid and trifluoromethanesulfonic acid were used as protic acids. Reactions of $[\mathbf{3}]PF_6$ used as the starting complex with hydrochloric acid afforded a new nitrosyl complex exhibiting a strong ν(NO) band at 1928 cm^{-1}; reversible and irreversible waves at −0.43 and −0.78 V, respectively; and the *trans*-(NO, Cl), *cis*-(Cl, Cl) configuration of $[RuCl_2(NO)(terpy)]^+$ around the ruthenium center ($[\mathbf{5}]^+$). The materials obtained under various conditions consisted of the starting complex ($[\mathbf{3}]^+$) and another nitrosyl complex such as $[\mathbf{1}]^+$ and $[RuCl(OH)(NO)(terpy)]^+$: Reactions of $[\mathbf{3}]^+$ afforded the isomeric pair of $[\mathbf{1}]^+$ and $[\mathbf{5}]^+$ under refluxing conditions, a mixture of $[\mathbf{3}]^+$ and $[\mathbf{5}]^+$ at low temperature, and a mixture of $[\mathbf{5}]^+$ and $[RuCl(OH)(NO)(terpy)]^+$ in low concentration hydrochloric acid under refluxing conditions. Thus, synthesis of $[\mathbf{5}]^+$ is successful by reaction of the alkoxo complex as the starting complex with 10 min of refluxing.

Trifluoromethanesulfonic acid was used for reactions of $[\mathbf{3}]PF_6$ in CH_3CN or H_2O under several different conditions. The reaction in CH_3CN afforded $[RuCl(CH_3CN)(NO)(terpy)]^{2+}$ ($[\mathbf{6}]^{2+}$), and that in H_2O afforded $[RuCl(OH)(NO)(terpy)]^+$, as the coordination ability of $CF_3SO_3^-$ is weaker than those of CH_3CN and H_2O. Structural analysis of $[\mathbf{6}]^{2+}$ revealed that the chloro ligand moved from the trans position to the cis position with respect to the nitrosyl ligand, i.e., gave the *trans*-(NO, Cl), *cis*-(CH_3CN, Cl) configuration around the Ru atom. This configuration of $[\mathbf{6}]^{2+}$ is explained by the π-acceptor character of the acetonitrile ligand, which prefers to coordinate at the cis position with respect to the nitrosyl ligand. Thus, reactions of alkoxonitrosyl complexes with trifluoromethanesulfonic acid are useful for the synthesis of nitrosyl complexes having the expected coexisting ligands and configuration around the Ru atom considering the nature of the solvent and the coexisting substrate.

Comparison of Isomers of $[RuCl_2(NO)(terpy)]^+$ and Related Complexes. *trans*-(NO, Cl), *cis*-(Cl, Cl)-$[RuCl_2(NO)(terpy)]Cl$ was synthesized by Reedijk et al. and characterized by spectroscopy and DFT calculations.[12] In this work, the PF_6 salt of *trans*-(NO, Cl), *cis*-(Cl, Cl)-$[RuCl_2(NO)(terpy)]^+$ ($[\mathbf{5}]^+$) was synthesized by an alternative synthetic route using the reactions of alkoxonitrosyl complexes with an acid. This isomer, $[\mathbf{5}]^+$, also formed in the synthetic reaction of the *trans*-(Cl, Cl), *cis*-(NO, Cl) isomer ($[\mathbf{1}]^+$) from $[RuCl_5(NO)]^{2-}$ as a minor product.[25] Reactions of $[\mathbf{1}]PF_6$ with KCl or HCl in aqueous solution under refluxing conditions afforded a mixture of these two isomers of $[RuCl_2(NO)(terpy)]^+$. An aqueous solution of $[\mathbf{1}]PF_6$ or

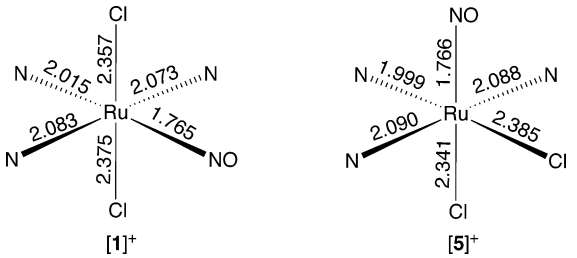


Figure 5. Structural comparison between bond lengths of $[\mathbf{1}]^+$ and $[\mathbf{5}]^+$ (in Å).

$[\mathbf{5}]PF_6$ in the presence of Cl^- (KCl and HCl) was heated to give a mixture of both isomers, $[\mathbf{1}]^+$ and $[\mathbf{5}]^+$, with a small amount of $[RuCl(OH)(NO)(terpy)]^+$, which was monitored by ^1H NMR spectroscopy (Figure S3) and CV. In the absence of Cl^-, the amount of $[RuCl(OH)(NO)(terpy)]^+$ increases, whereas the amounts of the isomers decrease. Thus, there is no significant difference in reactivity and stability between the isomers of $[RuCl_2(NO)(terpy)]^+$, $[\mathbf{1}]^+$ and $[\mathbf{5}]^+$, in solution. In fact, whereas the IR spectra of $[\mathbf{1}]PF_6$ and $[\mathbf{5}]PF_6$ in KBr disks show strong ν(NO) bands at 1895 and 1928 cm^{-1}, respectively, their ν(NO) bands are observed at the same frequency in CH_3CN solution. Cyclic voltammograms of both complexes show a reversible wave in the same region around −0.5 V, although the irreversible waves appear at −1.01 for $[\mathbf{1}]^+$ and −0.78 V for $[\mathbf{5}]^+$ (Figure S5). The frequency of ν(NO) and the reduction potential of the $(RuNO)^{3+}$ moiety are good indicators of the reactivity and stability of the nitrosyl complexes.[4,20,21,24] For this terpy series of nitrosyl complexes, the ν(NO) values in CH_3CN are a better indicator than those in KBr disks.

The structural parameters of the two isomers show a characteristic difference because of the strong trans effect of the nitrosyl ligand, which has a strong π-acceptor character (see Figure 5). The N−O distance of the *trans*-(NO, Cl), *cis*-(Cl, Cl) form, $[\mathbf{5}]^+$ [1.142(7) Å], is greater than that of the *trans*-(Cl, Cl), *cis*-(NO, Cl) form, $[\mathbf{1}]^+$ [1.129(4) Å], because of the difference between the weak π-donor Cl^- ligand and the π-acceptor py ligand at the trans position with respect to the nitrosyl ligand. The difference between the two Ru−Cl distances of *trans*-(NO, Cl), *cis*-(Cl, Cl)-$[\mathbf{5}]^+$ [2.341(2) Å at the trans position with respect to NO and 2.385(2) Å for the cis position] is greater than that of *trans*-(Cl, Cl), *cis*-(NO, Cl)-$[\mathbf{1}]^+$ [2.357(1) and 2.375(1) Å]. The Ru−Cl distances of the ruthenium complexes containing the terpy ligand are 2.39−2.46 Å.[15,16,18,25,27,35] There is a marked trans effect of the NO ligand toward the chloro ligand. The structural parameters of the terpy ligands of the two isomers in Table 3 are similar to those of ruthenium complexes containing the terpy ligand (Ru−N of the central N atom of the terpy 1.892−2.024 Å, that of the terminal N atoms is 2.053−2.154 Å, and the N−Ru−N angle is 78.1−80.8°).

Conclusions

The synthesis of ruthenium complexes containing nitrosyl and terpy ligands and their geometrical configuration around the ruthenium center have been studied. Reactions of $[\mathbf{1}]PF_6$ with NO_2^- and Br^- in H_2O or CH_3OH afford a *trans*-(NO, OR), *cis*-(X, OR)-type complex in which the OR ligand comes from the solvent. Synthesis of a nitrosylruthenium complex having the expected geometrical configuration was carried out by reactions of alkoxo complexes ($[\mathbf{3}]PF_6$) with a protic acid to dissociate the alkoxo ligand into an alcohol. $[\mathbf{5}]PF_6$ was formed by reaction with hydrochloric acid and characterized by X-ray crystallography. This complex was obtained as a mixture with $[\mathbf{1}]PF_6$ and was synthesized as a Cl salt using an alternative route by Reedijk et al.[12] The reaction of $[\mathbf{3}]PF_6$ with CF_3SO_3H in CH_3CN affords $[\mathbf{6}]^{2+}$, whose structure was determined by X-ray crystallography. These reactions occur via formation of an alcohol ligand by protonation to the alkoxo ligand and substitution by an entering ligand. The strong π-acceptor character of the nitrosyl ligand is indicated by comparison of the structural parameters between these complexes and related complexes, in particular between the isomeric pairs of $[RuCl_2(NO)(terpy)]^+$ moieties. The structural configurations of these reaction products are related to the nature of the entering ligand, and the decreasing order of tendency to coordinate at the trans position with respect to the nitrosyl ligand is $OH^- \approx OR^- > py(terpy) \approx Cl^- > Br^- > CH_3CN$. The configuration around the metal center containing the nitrosyl complex is controlled by the combination of ancillary ligands.

Supporting Information Available: NMR spectra, cyclic voltammograms, electronic spectra, and X-ray crystallographic data of $[\mathbf{3}]PF_6$, $[\mathbf{4}]PF_6 \cdot CH_3CN$, $[\mathbf{5}]CF_3SO_3$, and $[\mathbf{6}](PF_6)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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