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Reactions of Ruthenium Complexes Having Pyridyl-Containing Ligands, 2-Pyridinecarboxylato and 2,2′-Bipyridine, with an Azide Ion: Formation of Nitrido-Bridged Diruthenium Complexes

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Reactions of ruthenium complexes having 2-pyridinecarboxylato and 2,2′-bipyridine ligands with sodium azide in alcohol afforded nitrido-bridged diruthenium complexes, $[\{Ru(OR)(pyca)(bpy)\}_2(\mu\text{-}N)]^+$ ($R = CH_3, C_2H_5$). Diruthenium complexes showed diamagnetic properties, a linear Ru−N−Ru coordination configuration, and two irreversible oxidation waves and two reversible reduction waves.

Nitric oxide (NO) is an important molecule that functions as a signaling and/or regulating moiety in biological systems,[1] and η^1-nitric oxide (nitrosyl) coordinates to a metal center as linear and bent types showing different physical properties and various reactivities.[2] We have been investigating regulation of the geometry and reactivity of nitrosylruthenium complexes by nature of supporting pyridyl-containing ligands such as pyridine (py), 2,2′-bipyridine (bpy), 2-pyridinecarboxylate ion (pyca), and 2,2′:6′,2″-terpyridine.[3] The nitrosyl ligand linearly coordinating to a ruthenium center shows characteristic reactions toward nucleophiles such as OH^-, CH_3O^-, and N_3^-.[2,4] In this study, a new nitrosylruthenium complex having both pyca and bpy, *cis*-$[RuCl(NO)(pyca)(bpy)]^+$, was synthesized for the purpose of regulating the reactivity of ruthenium complexes. Reactions of the complex with NaN_3 in methanol and ethanol afforded unexpected nitrido-bridged dinuclear ruthenium complexes, $[\{Ru(OR)(pyca)(bpy)\}_2(\mu\text{-}N)]^+$ ($R = CH_3, C_2H_5$). These nitrido-bridged complexes were also obtained by reactions of a dichlororuthenium(III) complex, $[RuCl_2(pyca)(bpy)]$, with NaN_3. This paper describes that the reactivity toward N_3^- is dependent on the composition of supporting pyridyl-containing ligands. Some nitrido-bridged diruthenium complexes have been synthesized by reactions using ammonia, nitric acid, and terminal nitrido complexes as a nitrogen source,[5,6] and other metal complexes having a bridging nitrido ligand have been reported.[7] The formation of terminal and bridging nitridoruthenium complexes using N_3^- as a nitrido source has also been reported.[8,9]

A new nitrosyl complex having mixed supporting ligands of pyca and bpy, *cis*-$[RuCl(NO)(pyca)(bpy)]PF_6$, was prepared by the reaction of $Et_4N[RuCl_3(NO)(pyca)]$ with bpy in $H_2O\text{-}(CH_3)_2CO$ under refluxing conditions followed by the addition of NH_4PF_6 as a precipitant.[10] Reactions of *cis*-$[RuCl(NO)(pyca)(bpy)]PF_6$ with NaN_3 in several solvents were carried out to synthesize new complexes. Reaction of the $\{RuNO\}^6$-type nitrosyl complex with NaN_3 is a well-known reaction of a nitrosyl ligand and affords a solvento

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(1) (a) Ignarro, J. N. *Nitric Oxide: Biology and Pathobiology*; Academic Press: San Diego, CA, 2000. (b) Miranda, K. M. *Coord. Chem. Rev.* **2005**, *249*, 433. (c) Szacilowski, K.; Chmura, A.; Stasicka, Z. *Coord. Chem. Rev.* **2005**, *249*, 2408.

(2) (a) Richter-Addo, G. B.; Legdzins, P. *Metal Nitrosyls*; Oxford: New York, 1992. (b) Roncaroli, F.; Videla, M.; Sleo, L. D.; Olabe, J. A. *Coord. Chem. Rev.* **2007**, *251*, 1903. (c) Richter-Addo, G. B., Legdzins, P., Burstyn, J., Eds. Nitric Oxide Chemistry. In *Chemical Review*; American Chemical Society: Washington, DC, 2002; p 102.

(3) (a) Fukui, S.; Shimamura, Y.; Sunamoto, Y.; Abe, T.; Hirano, T.; Oi, T.; Nagao, H. *Polyhedron* **2007**, *26*, 4645. (b) Nagao, H.; Enomoto, K.; Wakabayashi, Y.; Komiya, G.; Hirano, T.; Oi, T. *Inorg. Chem.* **2007**, *46*, 1431. (c) Hirano, T.; Oi, T.; Nagao, H.; Morokuma, K. *Inorg. Chem.* **2003**, *42*, 6575. (d) Ooyama, D.; Nagao, N.; Nagao, H.; Miura, Y.; Hasegaea, A.; Ando, K.; Howell, F. S.; Mukaida, M.; Tanaka, K. *Inorg. Chem.* **1995**, *34*, 6024.

(4) (a) Parkash, R.; Götz, A. W.; Heinemann, F. W.; Görling, A.; Sellmann, D. *Inorg. Chem.* **2006**, *45*, 4661. (b) Roncaroli, F.; Olabe, J. A. *Inorg. Chem.* **2005**, *44*, 4719.

(5) (a) Cleare, M. J.; Griffith, W. P. *J. Chem. Soc. A* **1970**, 1117. (b) Campbell, J. R.; Clark, R. J. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1239.

(6) (a) Haukka, M.; Ahlgrén, M.; Pakkanen, T. A. *Inorg. Chem.* **1995**, *34*, 2931. (b) Bonomo, L.; Solari, E.; Scopelliti, R.; Floriani, C. *Angew. Chem., Int. Ed.* **2001**, *40*, 2529. (c) Yip, K.-L.; Yu, W.-Y.; Chan, P.-M.; Zhu, N.-Y.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **2003**, 3556.

(7) (a) Brown, S. D.; Peters, J. C. *J, Am. Chem. Soc.* **2005**, *127*, 1919. (b) Meyer, K.; Bill, E.; Mienert, B.; Weyhermueller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **1999**, *121*, 4859. (c) Niemann, A.; Bossek, U.; Haselhorst, G.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1996**, *35*, 906. (d) Ercolani, C.; Hewage, S.; Heucher, R.; Rossi, G. *Inorg. Chem.* **1993**, *32*, 2975.

(8) Griffith, W. P.; Pawson, D. *J. Chem. Soc., Dalton Trans.* **1973**, 1315.

(9) (a) Rossi, G.; Gardini, M.; Pennesi, G.; Ercolani, C.; Goedken, V. L. *J. Chem. Soc., Dalton Trans.* **1989**, 193. (b) Jüstel, T.; Bendix, J.; Metzler-Nolte, N.; Weyhermüller, T.; Nuber, B.; Wieghardt, K. *Inorg. Chem.* **1998**, *37*, 35. (c) Sellman, D.; Gottschalk-Gaudig, T.; Heinemann, F. W. *Inorg. Chim. Acta* **1998**, *269*, 63.

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complex with evolution of N_2O and N_2.[11] *cis*-$[RuCl(NO)(pyca)(bpy)]^+$ and the corresponding bis(bpy)-type complex reacted with equimolar ammounts of NaN_3 in CH_3CN to afford $[RuCl(CH_3CN)L(bpy)]^{n+}$ (L = pyca; $n = 0$, L = bpy; $n = 1$; eq 1) with $[Ru(CH_3CN)_2L(bpy)]^{(n+1)+}$.

$$[RuCl(NO)L(bpy)]^{(n+1)+} + N_3^- + CH_3CN \rightarrow [RuCl(CH_3CN)L(bpy)]^{n+} + N_2O + N_2 \quad (1)$$

Reactions of *cis*-$[RuCl(NO)(pyca)(bpy)]PF_6$ with an excess amount of NaN_3 in CH_3OH or C_2H_5OH under refluxing conditions gave new diruthenium complexes $[\{Ru(OR)(pyca)(bpy)\}_2(\mu\text{-}N)]PF_6$ (R = CH_3, C_2H_5),[12,13] with evolving N_2O and N_2, which was confirmed by gas chromatography. Those of the corresponding bis(bpy)-type complex afforded $[Ru^{II}(N_3)_2(bpy)_2]$, which was stable in these solvents and reacted with oxidizing agents to undergo decomposition or CH_3I in CH_3CN to afford an imineruthenium(II) complex, $[Ru(NH{=}CH_2)(CH_3CN)(bpy)_2]^{2+}$.[14,15]

The new ethoxo- and methoxonitrido-bridged complexes respectively showed ν(Ru−N−Ru) bands at 1018 and 1017 cm^{-1} in the IR spectrum (Figure S1 in the Supporting Information). The cyclic voltammograms in CH_3CN revealed both two irreversible oxidation waves at 0.96 and 1.29 V for the ethoxo complex and 1.05 and 1.38 V for the methoxo complex and two reversible reduction waves at −1.38 and −1.52 V for the ethoxo complex and −1.35 and −1.48 V for the methoxo complex (Figures 1 and S3 in the Supporting Information). ^1H and ^{13}C NMR signals of these complexes were observed in the normal regions, and these spectra revealed their diamagnetic properties (Figures S5 and S6 in the Supporting Information).[5] Single crystals of the methoxo complex suitable for X-ray structural analysis were obtained by the slow diffusion of diethyl ether into a CH_3CN-H_2O solution. The structure of $[\{Ru(OCH_3)(pyca)(bpy)\}_2(\mu\text{-}N)]^+$ is shown in Figure 2.[16] The nitrido nitrogen atom connected the two ruthenium units to form a linear dinuclear complex, with the Ru−N−Ru angle equal to 176.9(2)°. The geometry around each ruthenium center was distorted octahedral with four nitrogen atoms of the nitrido, bpy, and pyca ligands and two oxygen atoms of the alkoxo and pyca ligands. Bond lengths of Ru−N(nitrido), 1.735(3) and 1.744(3) Å, were similar to those of the reported nitridoruthenium complexes, 1.728−1.764 Å.[9,17] The bonds between Ru and O(pyca), 2.086(3) and 2.073(3) Å, were elongated because of the trans influence of the bridging nitrido ligand, which functioned as a strong π donor.

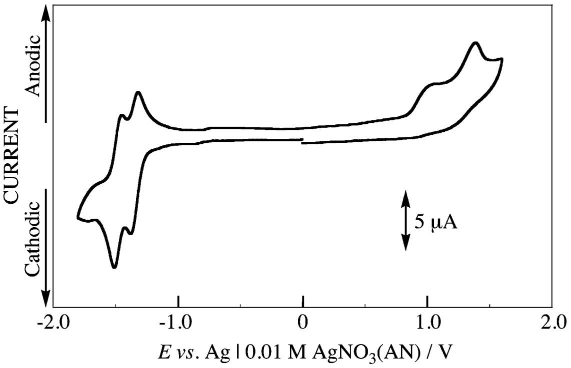

Figure 1. Cyclic voltammogram of $[\{Ru(OCH_3)(pyca)(bpy)\}_2(\mu\text{-}N)]PF_6$ in CH_3CN at −40 °C.

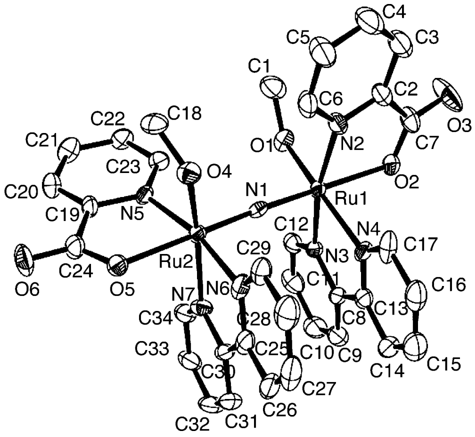

Figure 2. Structure of $[\{Ru(OCH_3)(pyca)(bpy)\}_2(\mu\text{-}N)]^+$ with atom labels. Hydrogen atoms are omitted for clarity.

The origin of the nitrido nitrogen atom in the diruthenium complex has been examined using ^{15}N-labeled $[RuCl(^{15}NO)(pyca)(bpy)]PF_6$ and ^{15}N-labeled sodium azide,

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(10) Yield: 87%. Anal. Found: C, 32.74; H, 2.04; N, 9.43. Calcd for $[RuCl(NO)(pyca)(bpy)]PF_6$: C, 32.58; H, 2.05; N, 9.50. FAB-MS (*m/z*): 445 (M − PF_6). IR (KBr): ν(NO) 1901 cm^{-1}. ^1H NMR (500 MHz, CD_3CN, Me_4Si): δ 7.65 (dd, *J* = 5.8 and 5.8 Hz, 1H), 7.95 (dd, *J* = 5.8 and 5.8 Hz, 1H), 8.00 (d, *J* = 5.8 Hz, 1H), 8.07 (dd, *J* = 5.5 and 5.5 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 8.37−8.42 (m, 2H), 8.50 (dd, *J* = 8.2 and 7.6 Hz, 1H), 8.60 (dd, *J* = 8.2 and 8.2 Hz, 2H), 8.86 (d, *J* = 5.5 Hz, 1H), 9.47 (d, *J* = 5.5 Hz, 1H). ^{13}C NMR (CD_3CN): δ 126.01, 126.10, 129.37, 129.44, 129.57, 132.36, 143.86, 144.31, 144.51, 149.97, 152.09, 152.40, 153.01, 155.98, 156.83, 178.51.

(11) Bottomley, F. *Acc. Chem. Res.* **1978**, *11*, 158.

(12) Yield: 51%. Anal. Found: C, 39.43; H, 3.61; N, 9.15. Calcd for $[\{Ru(OC_2H_5)(pyca)(bpy)\}_2(\mu\text{-}N)]PF_6\cdot 5H_2O$: C, 39.38; H, 4.04; N, 8.93. FAB-MS (*m/z*): 864 (M − PF_6), 774 (M − PF_6 − $2OC_2H_5$). IR: ν(Ru−N−Ru) 1018 cm^{-1}. ^1H NMR (500 MHz, CD_3CN, Me_4Si): δ 1.34 (dd, *J* = 6.9 and 6.9 Hz, 6H), 3.47 (dq, *J* = 9.2 and 6.9 Hz, 2H), 3.57 (dq, *J* = 9.2 and 6.9 Hz, 2H), 6.92 (dd, *J* = 5.5 and 5.5 Hz, 2H), 7.02 (d, *J* = 5.5 Hz, 2H), 7.81 (dd, *J* = 7.8 and 5.5 Hz, 2H), 7.94 (d, *J* = 7.8 Hz, 2H), 7.99−8.04 (m, 6H), 8.09 (d, *J* = 7.8 Hz, 2H), 8.15 (dd, *J* = 7.8 and 7.8 Hz, 2H), 8.27 (dd, *J* = 7.8 and 7.8 Hz, 2H), 9.64 (d, *J* = 5.5 Hz, 2H), 10.11 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (CD_3CN, Me_4Si): δ 21.03, 66.75, 125.17, 125.22, 128.39, 128.68, 129.35, 130.32, 142.10, 142.18, 142.58, 150.30, 150.55, 153.37, 155.47, 156.40, 157.51, 169.79.

(13) (13) Yield: 28%. Anal. Found: C, 40.75; H, 3.07; N, 9.79. Calcd for $[\{Ru(OCH_3)(pyca)(bpy)\}_2(\mu\text{-}N)]PF_6\cdot 2H_2O$: C, 40.20; H, 3.37; N, 9.65. FAB-MS (*m/z*): 836 (M − PF_6). IR: ν(Ru−N−Ru) 1017 cm^{-1}. ^1H NMR (500 MHz, CD_3CN, Me_4Si): δ 3.48 (s, 6H), 6.89 (dd, *J* = 5.5 and 5.2 Hz, 2H), 7.07 (d, *J* = 5.5 Hz, 2H), 7.71 (dd, *J* = 7.8 and 5.5 Hz, 2H), 7.92 (d, *J* = 7.8 Hz, 2H), 8.00 (d, *J* = 5.2 Hz, 4H), 8.08−8.12 (m, 6H), 8.29 (dd, *J* = 7.8 and 7.8 Hz, 2H), 9.50 (d, *J* = 5.5 Hz, 2H), 9.98 (d, *J* = 5.2 Hz, 2H). ^{13}C NMR (CD_3CN): δ 59.67, 118.20, 125.04, 125.09, 128.33, 128.51, 129.19, 130.72, 142.01, 142.14, 142.54, 150.40, 153.09, 155.27, 156.16, 156.98, 169.70.

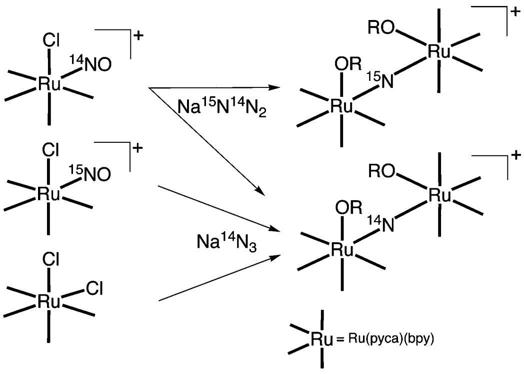
(14) Brown, G. M.; Callahan, R. W.; Meyer, T. J. *Inorg. Chem.* **1975**, *14*, 1915.

(15) Nagao, H.; Kikuchi, T.; Inukai, M.; Ueda, A.; Oi, T.; Suzuki, N.; Yamasaki, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3131.

(16) Crystal data for $[\{Ru(OCH_3)(pyca)(bpy)\}_2(\mu\text{-}N)]PF_6\cdot 2H_2O$: monoclinic, $P2_1/c$, $a = 14.743(4)$ Å, $b = 12.996(4)$ Å, $c = 19.824(6)$ Å, $\beta = 92.3280(11)°$, $V = 3795.1(20)$ Å^3, $Z = 4$, λ(Mo Kα) = 0.710 70 Å, $T = 93$ K, 29 195 reflections collected, 8683 unique ($R_{int} = 0.048$), R1 = 0.0635, wR2 = 0.2243 [$I > 2\sigma(I)$]. CCDC 688231.

(17) (a) Griffith, W. P.; Mockford, M. J.; Skapski, A. C. *Inorg. Chim. Acta* **1987**, *126*, 179. (b) Haukka, M.; Ahlgrén, M.; Pakkanen, T. A. *Inorg. Chem.* **1995**, *34*, 2931. (c) Haukka, M.; Venäläinen, T.; Ahlgrén, M.; Pakkanen, T. A. *J. Chem. Soc., Dalton Trans.* **1996**, 1927. (d) Sun, X.-R.; Liang, J.-L.; Che, C.-M.; Zhu, N.; Zhang, X. X.; Gao, S. *J. Chem. Soc., Chem. Commun.* **2002**, 2090.

Scheme 1. Formation of Nitrido-Bridged Diruthenium Complexes



$Na^{15}N^{14}N_2$ (99% atom ^{15}N), in C_2H_5OH according to the above procedure. For the reaction of $[RuCl(^{14}NO)(pyca)(bpy)]PF_6$ with $Na^{15}N^{14}N_2$, two IR bands were observed at 1018 and 995 cm^{-1}. The IR characteristic bands of the ν(Ru−N−Ru) mode at 1018 and 995 cm^{-1} were assigned to $\nu(Ru-^{14}N-Ru)$ and $\nu(Ru-^{15}N-Ru)$, respectively (Figure S2 in the Supporting Information). For the reaction of $[RuCl(^{15}NO)(pyca)(bpy)]PF_6$ with $Na^{14}N_3$, the IR spectrum showed only the band at 1018 cm^{-1}. These results indicated that the source of the bridged nitrido nitrogen atom was an azide ion (Scheme 1).

The formation reaction of the nitrido-bridged diruthenium complex appeared to proceed via oxidation of the ruthenium(II) species, which formed by a nucleophilic attack of N_3^- to the nitrosyl ligand according to eq 1. Isolation of the reaction intermediates such as a solvento or N_3-adducted complex so far has been unsuccessful. The nitrido-bridged complex was also synthesized in a good yield by the reaction of $[Ru^{III}Cl_2(pyca)(bpy)]$, which was synthesized by the ruthenium blue method.[18] These synthetic reactions also occurred under an argon atmosphere and in the dark, while the reaction using $[Ru^{II}(CH_3CN)_2(pyca)(bpy)]PF_6$ afforded an unidentified mixture, which did not contain the nitrido-bridged complex. The nitrido-bridged diruthenium complex formed by N_2 evolution, followed by an intramolecular electron transfer between ruthenium and nitrogen bridging units, gave a $Ru^{IV}-N^{3-}-Ru^{IV}$ moiety. The alkoxo ligands functioned as stabilizers for high oxidation states of the ruthenium centers.

In conclusion, azide ions function as a nitrogen source to form the nitrido-bridged diruthenium complex in reactions of the pyca−bpy mixed-ligand-type ruthenium complexes. Reactions using bis(bpy)-type complexes such as $[RuCl_2(bpy)_2]^+$ and $[RuCl(NO)(bpy)_2]^{2+}$ were carried out under similar conditions to afford the bis(azido) complex, $[Ru(N_3)_2(bpy)_2]$ in high yield. The difference in reactivity toward N_3^- between the pyca−bpy mixed-ligand and bis(bpy)-type complexes should be emphasized. The formation of the nitrido-bridged diruthenium complex is due to stability of the ruthenium(III) state with an electron-donor 2-pyridinecarboxylato as the supporting ligand. Thus, reactivity of the azido ligand on the ruthenium center was regulated by the combination of supporting ligands such as bpy and pyca. The present reaction is important as a synthetic route of nitrogen-containing complexes using an azide ion as the nitrogen source. Further details of the reaction and synthesis of new nitrido-bridged diruthenium complexes are in progress.

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Supporting Information Available: Syntheses of ruthenium complexes, characterization data of $[\{Ru(OR)(pyca)(bpy)\}_2(\mu-N)]PF_6$, and crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] Yield: 36%. Anal. Found: C, 44.40; H, 3.40; N, 8.15. Calcd for $[RuCl_2(pyca)(bpy)]\cdot(CH_3)_2CO$: C, 44.89; H, 3.57; N, 8.27. FAB-MS (*m*/*z*): 451 (M + H^+), 415 (M − Cl).