Synthesis and Structure of Novel Zerovalent Ruthenium Complexes with Three Pyridine Ligands or Tridentate Pyridyl Ligands

Masashi Shiotsuki, Toshiaki Suzuki, Kazuo Iida, Yasuyuki Ura, Kenji Wada, Teruyuki Kondo, and Take-aki Mitsudo*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

Received October 21, 2002

Ru(η^6-cot)(dmfm)$_2$ (**1**; cot = 1,3,5-cyclooctatriene, dmfm = dimethyl fumarate), which is easily derived from Ru(1−2:5−6-η-cod)(η^6-cot) (cod = 1,5-cyclooctadiene), reacts with an excess amount of pyridine to give a novel ruthenium(0) complex, Ru(dmfm)$_2$(pyridine)$_3$ (**4**). Complex **1** reacts with tridentate pyridyl ligands (N-N′-N) such as 2,2′:6′,2″-terpyridine (terpy), 2,6-bis(imino)pyridyl ligands, and 2,6-bis[(4*S*)-(−)-isopropyl-2-oxazolin-2-yl]pyridine (*i*-Pr-Pybox) to give novel ruthenium(0) complexes, Ru(dmfm)$_2$(N-N′-N). The products are mixtures of two isomers, respectively, one of which is different from the other by the coordinating enantioface of a dmfm ligand. The structures of **4** and one of the isomers of Ru(dmfm)$_2$-(terpy) (**5**) and Ru(dmfm)$_2$(*i*-Pr-Pybox) (**8**) were elucidated by X-ray analysis.

Introduction

Strong σ-donor nitrogen ligands have been revealed to be congenial to transition metals. Particularly, transition metal complexes having pyridine-based ligands have been thoroughly studied. As for ruthenium, various complexes with polypyridyl ligands (for instance, 2,2′:6′,2″-terpyridine and its derivatives[1]) have been well investigated because of their interesting photochemical and redox properties.[2] Other tridentate ligands such as 2,6-bis(imino)pyridine and Pincer-type ligands have been disclosed to form ruthenium complexes,[3−9] some of which show catalytic activity in many important reactions, for example, epoxidation of cyclohexene,[7] cyclopropanation of styrene,[8] N-alkylation of aromatic amines with diols,[9] ring-opening metathesis polymerization of 2-norbornene,[10] and DNA cleavage.[11] The asymmetric tridentate nitrogen ligand 2,6-bis[(4*S*)-(−)-isopropyl-2-oxazolin-2-yl]pyridine (*i*-Pr-Pybox) is known to form ruthenium complexes that catalyze an asymmetric cyclopropanation of olefinic compounds with diazoacetates[12] and polymerization of ethylene.[13] These complexes are divalent or tetravalent ruthenium complexes, and, to the best of our knowledge, isolable mononuclear *zerovalent* ruthenium complexes with tridentate nitrogen ligands have not been reported and are expected to have unique reactivity.

Recently, we reported the first example of zerovalent ruthenium complexes with mono- and bidentate nitrogen ligands (L^1 and L^2, respectively) such as Ru(η^6-cot)-(dmfm)(L^1) (**2**;[14] L^1 = pyridine, propylamine, benzylamine, or dimethylamine, cot = 1,3,5-cyclooctatriene, dmfm = dimethyl fumarate) and Ru(1−2:5−6-η-cot)-(dmfm)(L^2) (**3**;[15] L^2 = 2,2′-bipyridyl or 1,10-phenanthroline). These complexes are easily derived from Ru(η^6-

* To whom correspondence should be addressed. E-mail: mitsudo@scl.kyoto-u.ac.jp.

(1) For a review of syntheses of polypyridyl ligands, see: Cargill-Tompson, A. M. W. *Coord. Chem. Rev.* **1997**, *160*, 1.

(2) For reviews of photochemical and redox properties of polypyridyl ligands, see: (a) Kurihara, M.; Nishihara, H. *Coord. Chem. Rev.* **2002**, *226*, 125. (b) De Cola, L.; Belser, P. *Coord. Chem. Rev.* **1998**, *177*, 301. (c) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759. (d) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.

(3) (a) Dias, E. L.; Brookhart, M.; White, P. S. *Organometallics* **2000**, *19*, 4995. (b) Poon, C.-K.; Che, C.-M. *J. Chem. Soc., Chem. Commun.* **1979**, 861.

(4) (a) Beerens, H. I.; Wijkens, P.; Jastrzebski, J. T. B. H.; Verpoort, F.; Verdonck, L.; van Koten, G. *J. Organomet. Chem.* **2000**, *603*, 244. (b) del Río, I.; van Koten, G.; Lutz, M.; Spek, A. L. *Organometallics* **2000**, *19*, 361. (c) del Río, I.; Back, S.; Hannu, M. S.; Rheinwald, G.; Lang, H.; van Koten, G. *Inorg. Chim. Acta* **2000**, *300*, 1094. (d) del Río, I.; Gossage, R. A.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **1999**, *583*, 69. (e) del Río, I.; Gossage, R. A.; Lutz, M.; Spek, A. L.; van Koten, G. *Inorg. Chim. Acta* **1999**, *287*, 113. (f) del Río, I.; Gossage, R. A.; Hannu, M. S.; Lutz, M.; Spek, A. L.; van Koten, G. *Organometallics* **1999**, *18*, 1097. (g) Abbenhuis, R. A. T. M.; del Río, I.; Bergshoef, M. M.; Boersma, J.; Veldman, N.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1998**, *37*, 1749.

(5) Gemel, C.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **2000**, *39*, 1593.

(6) Redmore, S. M.; Rickard, C. E. F.; Webb, S. J.; Wright, L. J. *Inorg. Chem.* **1997**, *36*, 4743.

(7) Çetinkaya, B.; Çetinkaya, E.; Brookhart, M.; White, P. S. *J. Mol. Catal. A Chem.* **1999**, *142*, 101.

(8) Bianchini, C.; Lee, H. M. *Organometallics* **2000**, *19*, 1833.

(9) Abbenhuis, R. A. T. M.; Boersma, J.; van Koten, G. *J. Org. Chem.* **1998**, *63*, 4282.

(10) del Río, I.; van Koten, G. *Tetrahedron Lett.* **1999**, *40*, 1401.

(11) Welch, T. W.; Ciftan, S. A.; White, P. S.; Thorp, H. H. *Inorg. Chem.* **1997**, *36*, 4812.

(12) (a) Doyle, M. P.; Peterson, C. S.; Zhou, Q.-L.; Nishiyama, H. *Chem. Commun.* **1997**, 211. (b) Park, S.-B.; Sakata, N.; Nishiyama, H. *Chem. Eur. J.* **1996**, *2*, 303. (c) Nishiyama, H.; Itoh, Y.; Sugawara, Y.; Matsumoto, H.; Aoki, K.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1247. (d) Park, S.-B.; Murata, K.; Matsumoto, H.; Nishiyama, H. *Tetrahedron Asymmetry* **1995**, *6*, 2487. (e) Nishiyama, H.; Itoh, Y.; Matsumoto, H.; Park, S.-B.; Itoh, K. *J. Am. Chem. Soc.* **1994**, *116*, 2223

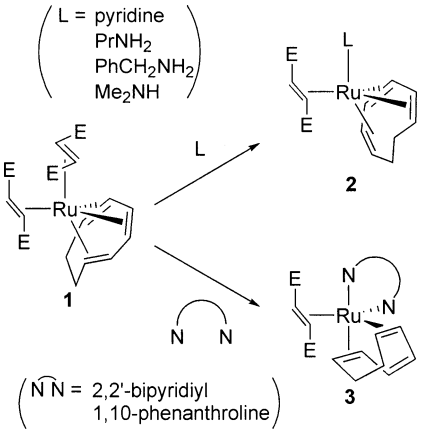
(13) (a) Imanishi, Y.; Nomura, K. *J. Polym. Sci. Polym. Chem.* **2000**, *38*, 4613. (b) Nomura, K.; Warit, S.; Imanishi, Y. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 599. (c) Nomura, K.; Warit, S.; Imanishi, Y. *Macromolecules* **1999**, *32*, 4732.

(14) Suzuki, T.; Shiotsuki, M.; Wada, K.; Kondo, T.; Mitsudo, T. *J. Chem. Soc., Dalton Trans.* **1999**, 4231.

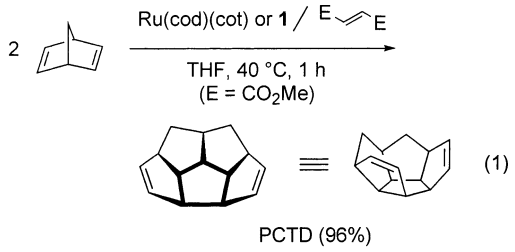
(15) Suzuki, T.; Shiotsuki, M.; Wada, K.; Kondo, T.; Mitsudo, T. *Organometallics* **1999**, *18*, 3671.

10.1021/om0208725 CCC: $25.00
Publication on Web 02/19/2003

Scheme 1. Reaction of 1 with Mono- or Bidentate Nitrogen Ligands



cot)(dmfm)$_2$ (**1**)[16] (Scheme 1). Complex **1** shows excellent catalytic activity in the unusual dimerization of 2,5-norbornadiene to give pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]-tetradeca-4,11-diene (PCTD) involving carbon−carbon bond cleavage and reconstruction of a novel carbon skeleton under very mild conditions (eq 1).[16] Complex **1** has been revealed to be a versatile starting material for preparation of various Ru(0) complexes.[14,15,17,18] We now report a series of novel zerovalent ruthenium complexes with three pyridine ligands and those with tridentate pyridyl ligands derived from **1**.



Results and Discussion

A pyridine solution of Ru(η^6-cot)(dmfm)$_2$ (**1**) was refluxed for 2 h to give Ru(dmfm)$_2$(pyridine)$_3$ (**4**) in 58% yield via the dissociation of the cot ligand in **1** followed by the coordination of three pyridine molecules (eq 2). It is noteworthy that no stereoisomer was included in the product of this reaction. Complex **4** is a zerovalent ruthenium complex with both σ-donor and π-acceptor ligands and follows the 18-electron rule. The ^{1}H NMR spectra of **4** exhibited two singlets (δ 3.36 and 2.98) corresponding to the methoxy groups of dmfm and an AB quartet (δ 4.23 and 3.97, J = 8.6 Hz) corresponding to the olefinic protons of dmfm. In the ^{1}H NMR spectrum of **4**, 11 nonequivalent protons for pyridine ligands were observed for these 15 protons, which means that two axial pyridine ligands are not equivalent to each other. Therefore, the structure of **4** in solution could have C_s symmetry. Thus, one of the two dmfm ligands in **4** coordinates with the (*re*, *re*) enantioface and the other with the (*si*, *si*) enantioface. This means that one of the dmfm ligands must dissociate once and re-coordinate to the ruthenium center.

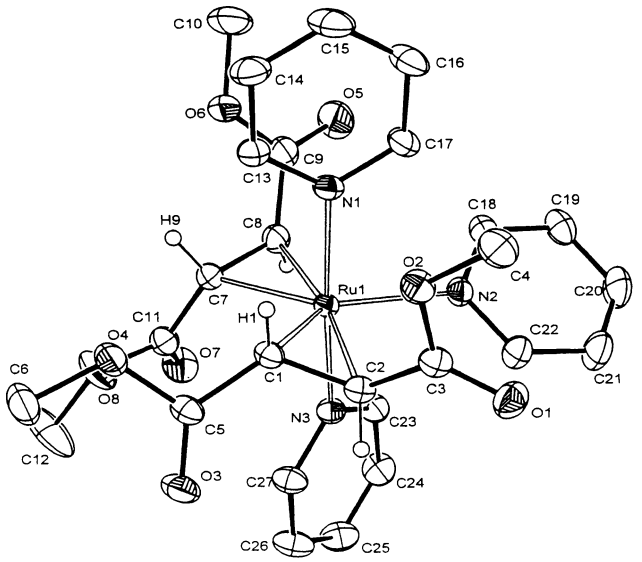
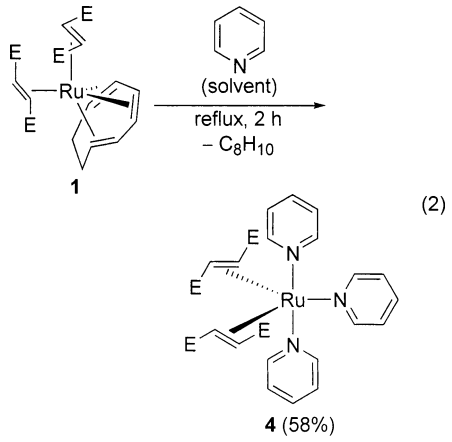


Figure 1. Structure of Ru(dmfm)$_2$(pyridine)$_3$·CH_2Cl_2 (**4**·CH_2Cl_2). CH_2Cl_2 and some hydrogen atoms are omitted for clarity. Thermal ellipsoids are given at the 30% probability level.



The structure of **4** was exactly confirmed by X-ray analysis (Figure 1). The crystal data and the details are given in Table 1. The structure of **4** is rationalized as a distorted trigonal bipyramid, in which three molecules of pyridine occupy two axial and one equatorial position, and two dmfm ligands are held in equatorial positions. The olefinic double bonds of the dmfm ligands lie in the equatorial plane.

The selected bond distances and angles are given in Tables 2 and 3, respectively. The angle of N(1)−Ru(1)−N(3) is 175.40(8)°, which implies that the coordinated N(1) and N(3) of the σ-donor ligands occupy axial positions. The axial Ru−N bond distances [Ru(1)−N(1) = 2.133(2) and Ru(1)−N(3) = 2.135(2) Å] are shorter than that of a monopyridine ruthenium(0) complex of **2** [Ru−N = 2.175(3) Å],[14] but are in the typical range for the Ru−N(pyridine) σ-bond of tripyridine ruthenium

(16) Mitsudo, T.; Suzuki, T.; Zhang, S.-W.; Imai, D.; Fujita, K.; Manabe, T.; Shiotsuki, M.; Watanabe, Y.; Wada, K.; Kondo, T. *J. Am. Chem. Soc.* **1999**, *121*, 1839.
(17) Shiotsuki, M.; Suzuki, T.; Kondo, T.; Wada, K.; Mitsudo, T. *Organometallics* **2000**, *19*, 5733.
(18) Shiotsuki, M.; Miyai, H.; Ura, Y.; Suzuki, T.; Kondo, T.; Mitsudo, T. *Organometallics* **2002**, *21*, 4960.

Table 1. Summary of Crystal Data, Collection Data, and Refinement of 4, 5b, and 10a

	4·CH_2Cl_2	**5b**·2{$(CH_3)_2CO$}	**10a**
empirical formula	$C_{27}H_{31}N_3O_8Ru$·CH_2Cl_2	$C_{27}H_{27}N_3O_8Ru$·2{$(CH_3)_2CO$}	$C_{29}H_{39}N_3O_{10}Ru$
fw	711.56	738.76	690.71
cryst color	brown	brown	black
habit	prismatic	prismatic	prismatic
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (#2)	$P2_1/c$ (#14)	$P2_1$ (#4)
a (Å)	10.830(6)	13.6929(9)	9.064(9)
b (Å)	15.52(1)	14.027(1)	17.019(5)
c (Å)	10.035(6)	18.8621(2)	10.776(5)
α (deg)	104.38(6)	90	90
β (deg)	105.46(5)	111.98(1)	110.86(4)
γ (deg)	82.78(5)	90	90
V (Å^3)	1571.8(2)	3359.4(5)	1553.3(2)
Z	2	4	2
D_{calcd} (g/cm^3)	1.503	1.461	1.477
μ(Mo Kα) (cm^{-1})	7.20	5.27	5.64
T (°C)	23.0	−160.0	23.0
$2\theta_{max}$ (deg)	55.0	55.0	55.0
no. of reflns measd	7581	35799	3991
no. of obsd reflns	7199	7531	3680
R^a (%)	2.8	5.4	8.5
$R_w{}^a$ (%)	3.0	10.0	9.9
GOF	1.40	1.21	1.2

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) for 4, 5b, and 10a

	4	**5b**	**10a**
Ru(1)−N(1)	2.133(2)	2.078(1)	2.13(2)
Ru(1)−N(2)	2.221(2)	2.002(1)	2.02(1)
Ru(1)−N(3)	2.135(2)	2.072(1)	2.16(2)
Ru(1)−C(1)	2.148(3)	2.163(2)	2.11(2)
Ru(1)−C(2)	2.194(3)	2.159(2)	2.13(2)
Ru(1)−C(7)	2.129(3)	2.154(2)	2.19(2)
Ru(1)−C(8)	2.172(3)	2.159(2)	2.20(2)

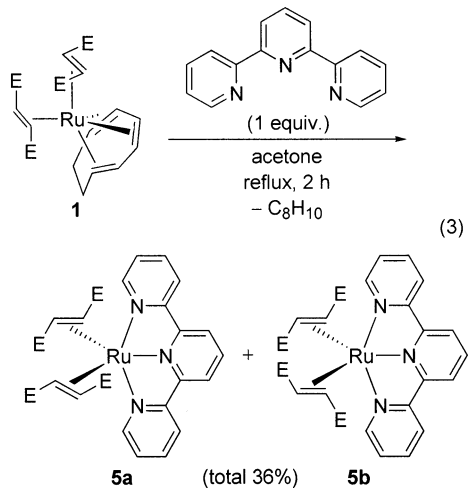
Table 3. Selected Bond Angles (deg) for 4, 5b, and 10a

	4	**5b**	**10a**
N(1)−Ru(1)−N(2)	92.2(1)	79.10(6)	78.5(6)
N(1)−Ru(1)−N(3)	175.40(8)	158.23(6)	153.3(7)
N(2)−Ru(1)−N(3)	83.9(1)	79.12(6)	74.8(5)
N(1)−Ru(1)−C(1)	82.1(1)	129.33(6)	93.8(7)
N(1)−Ru(1)−C(2)	94.9(1)	87.95(6)	97.8(6)
N(1)−Ru(1)−C(7)	93.1(1)	89.52(6)	87.8(6)
N(1)−Ru(1)−C(8)	88.6(1)	94.01(6)	95.7(7)
N(2)−Ru(1)−C(1)	130.01(9)	129.33(6)	128.1(6)
N(2)−Ru(1)−C(2)	93.4(1)	91.79(6)	91.4(7)
N(2)−Ru(1)−C(7)	133.89(9)	130.15(6)	133.4(6)
N(2)−Ru(1)−C(8)	95.4(1)	93.17(6)	97.8(6)
N(3)−Ru(1)−C(1)	102.3(1)	89.93(6)	104.0(7)
N(3)−Ru(1)−C(2)	87.8(1)	92.64(6)	84.8(7)
N(3)−Ru(1)−C(7)	87.8(1)	104.66(6)	109.3(6)
N(3)−Ru(1)−C(8)	89.2(1)	87.28(6)	86.2(7)

complexes.[19] The equatorial Ru−N bond distance [Ru(1)−N(2) = 2.221(2) Å] is exceptionally longer than the axial Ru−N bond distances. One reason for this difference would be the decrease of the electron density on the ruthenium atom by back-donation to the dmfm ligands. The same tendency was observed in the results of the X-ray analysis of the reported bipyridyl ruthenium(0) complex, **3**.[15]

A tridentate nitrogen ligand, 2,2′:6′,2″-terpyridine (terpy), was reacted with **1** in acetone under reflux for 2 h to afford a mixture of stereoisomers of a novel ruthenium(0) complex, Ru(dmfm)$_2$(terpy) (**5**), in 36% yield via the substitution between the cot ligand and terpy. In this reaction, the starting complex was completely consumed. The ^{1}H NMR spectrum of the reaction mixture showed that the selective formation of **5** was unsuccessful and a mixture of various complexes was formed. Using column chromatography, only complex **5** could be isolated. The obtained complexes were revealed to be a mixture of two stereoisomers, **5a** and **5b** in eq 3, based on the NMR spectra, and the ratio of **5a** to **5b** was 2.5:1. The structure of **5a** resembles that of **4**, but that of **5b** is different from those of **4** and **5a**; in **5a**, two dmfm ligands coordinate with the (*re*, *re*) and (*si*, *si*) enantiofaces, respectively, but in **5b**, both of the dmfm ligands coordinate with the same enantiofaces, (*si*, *si*) and (*si*, *si*) [or (*re*, *re*) and (*re*, *re*) in the enantiomer]. Thus, **5a** has a mirror plane containing all nitrogen atoms and the Ru center like **4**, while complex **5b** has a C_2 symmetry axis involving the Ru−N(central) bonds.

A number of ruthenium(II) complexes having a terpy ligand were reported so far.[2] Although the selective formation of one of the stereoisomers has not been achieved, **5a** and **5b** are the first example of an isolable mononuclear zerovalent ruthenium complex with a tridentate nitrogen ligand.



The structure of **5b** was confirmed by X-ray analysis. Single crystals of **5b** were obtained by recrystallization of the mixture of **5a** and **5b** from acetone/pentane. The ORTEP drawing of **5b** is displayed in Figure 2. The crystal data and the details are given in Table 1. The structure of **5b** is rationalized as a distorted trigonal bipyramid, in which the outer pyridyl moieties of terpy occupy axial coordination sites, and the central one is placed at an equatorial position. Both of the dmfm ligands are held in equatorial positions. These results indicate that the coordination number of **5b** is five, and

(19) For example, see; (a) Roche, S.; Adams, H.; Spey, S. E.; Thomas, J. A. *Inorg, Chem.* **2000**, *39*, 2385. (b) Stern, C.; Franceschi, F.; Solari, E.; Floriani, C.; Re, N.; Scopelliti, R. *J. Organomet. Chem.* **2000**, *593*, 86. (c) Laurent, F.; Plantalech, E.; Donnadieu, B.; Jiménez, A.; Hernández, F.; Martínez-Ripoll, M.; Biner, M.; Llobet, A. *Polyhedron* **1999**, *18*, 3321. (d) Fachinetti, G.; Funaioli, T.; Lecci, L.; Marchetti, F. *Inorg. Chem.* **1996**, *35*, 7217.

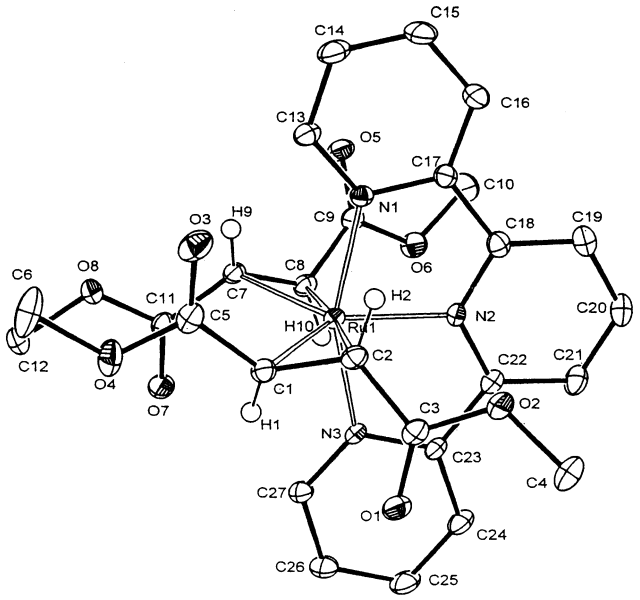
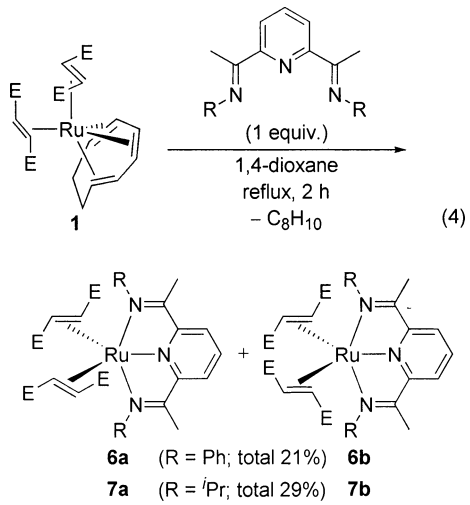


Figure 2. Structure of $Ru(dmfm)_2(terpy)\cdot 2\{(CH_3)_2CO\}$ [**5b**·2{$(CH_3)_2CO$}]. Two molecules of acetone [$(CH_3)_2CO$] and some hydrogen atoms are omitted for clarity. Thermal ellipsoids are given at the 50% probability level.

complex **5b** is a zerovalent ruthenium complex following the 18-electron rule.

The planes of three pyridyl groups are almost on the same plane. The bond angle of N(1)−Ru(1)−N(3) is 158.23(6)°. It is within the range [156.9(5)−159.8(1)°] observed for other ruthenium(II) complexes having a terpy ligand.[19c,20] The equatorial Ru−N bond distance [Ru(1)−N(2) = 2.002(1) Å] was shorter than that of the axial Ru−N bond [Ru(1)−N(1) = 2.078(1) Å and Ru(1)−N(3) = 2.072(1) Å], but is typical of Ru^{II}(terpy) complexes. This deviation is attributed to the geometrical constraints of the terpy backbone. These results point out that terpy holds the Ru atom tightly, and the ligand does not tend to dissociate from the Ru center.

A strong tridentate *σ*-donor ligand, 2,6-bis(imino)-pyridine (**NN′N**) such as 2,6-bis(1-phenyliminoethyl)-pyridine, was reacted with **1** in 1,4-dioxane under reflux for 2 h to give $Ru(dmfm)_2$(**NN′N**) (**6**) in 21% yield (eq 4). In a similar manner, 2,6-bis(1-isopropyliminoethyl)-pyridine reacted with **1** to afford an analogue **7** in 29% yield (eq 4). The products of these reactions were also a mixture of stereoisomers, one of which has two dmfm ligands coordinated with a combination of the same enantiofaces, and the other has two dmfm ligands coordinate with a combination of the (*si*, *si*) and (*re*, *re*) faces. The isolation of each isomer has not been achieved. The ratio of **6a** to **6b** was revealed to be 5.6:1, and that of **7a** to **7b** to be 3.7:1 by the ^{1}H NMR spectra.



Switching the coordinative enantioface of one of the dmfm ligands through this reaction suggests that the reaction would begin with the dissociation of the dmfm ligand (Scheme 2). The generated vacant site would be occupied by one of the terminal imine moieties to give the intermediate **8**. This is supposed on the basis of our report on the formation of ruthenium(0) complexes with monodentate nitrogen ligands.[14] Then the dissociation of the central olefinic group of the cot ligand is followed by the coordination of the central pyridyl group of the tridentate ligand to afford the intermediate **9**, according to the reported reaction pathway to form ruthenium(0) complexes having bidentate nitrogen ligands.[15] The dissociation of the 1,2-olefinic group of the cot ligand and the coordination of the last nitrogen moiety formed the Ru(N-N′-N) species. Finally, the dissociated dmfm ligand coordinates again in the place of the cot ligand with the (*si*, *si*) or (*re*, *re*) enantioface, which would produce stereoisomers such as **a** and **b** in Scheme 2. The cot ligand is not directly substituted by a tridentate nitrogen ligand. This mechanism would be able to explain the formation of the analogous complexes reported in this paper. In the case of **4**, however, the reason only one isomer could be obtained has not been clarified.

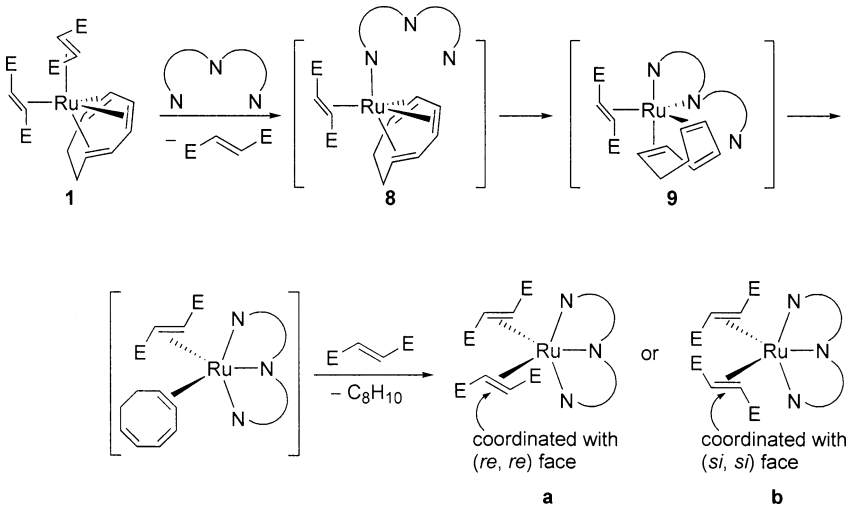
By using an asymmetric tridentate nitrogen ligand, 2,6-bis(oxazolinyl)pyridine (Pybox), successful enantioface-selective coordination of dmfm or *trans*-cyclooctene to ruthenium(II) was reported by Nishiyama et al.[21,22] Complex **1** reacted with 2,6-bis[(4*S*)-(−)-isopropyl-2-oxazolin-2-yl]pyridine (*i*-Pr-Pybox) in 1,2-dichloroethane under reflux for 2 h to afford a mixture of two stereoisomers of $Ru(dmfm)_2$(*i*-Pr-Pybox) (**10a**, and **10b** or **10c**) in good yield (Scheme 3). Although the selective formation of only one stereoisomer could not be achieved, the formation of the one isomer (**10b** or **10c**) could be successfully prevented. The ratio of **10a** to **10b** (or **10c**) was revealed to be 1:1 by the ^{1}H NMR spectrum. The structures of the products were deduced on the basis of ^{1}H, ^{13}C NMR and IR spectra. The structure of **10a** was

(20) For example, see: (a) Hirano, T.; Ueda, K.; Mukaida, M.; Nagao, H.; Oi, T. *J. Chem. Soc., Dalton Trans.* **2001**, 2341. (b) Hansongnern, K.; Saeteaw, U.; Cheng, J.; Liao, F.-L.; Lu, T.-H. *Acta Crystallogr.* **2001**, *C57*, 895. (c) Perez, W. J.; Lake, C. H.; See, R. F.; Toomey, L. M.; Churchill, M. R.; Takeuchi, K. J.; Radano, C. P.; Boyko, W. J.; Bessel, C. A. *J. Chem. Soc., Dalton Trans.* **1999**, 2281. (d) Heirtzler, F. R.; Neuburger, M.; Zehnder, M.; Bird, S. J.; Orrell, K. G.; Sik, V. *J. Chem. Soc., Dalton Trans.* **1999**, 565. (e) Gibson, D. H.; Sleadd, B. A.; Mashuta, M. S.; Richardson, J. F. *Organometallics* **1997**, *16*, 4421. (f) Sutter, J.-P., James, S. L.; Steenwinkel, P.; Karlen, T.; Grove, D. M.; Veldman, N.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1996**, *15*, 941. (g) Bardwell, D. A.; Cargill-Thompson, A. M. W.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1996**, 873.

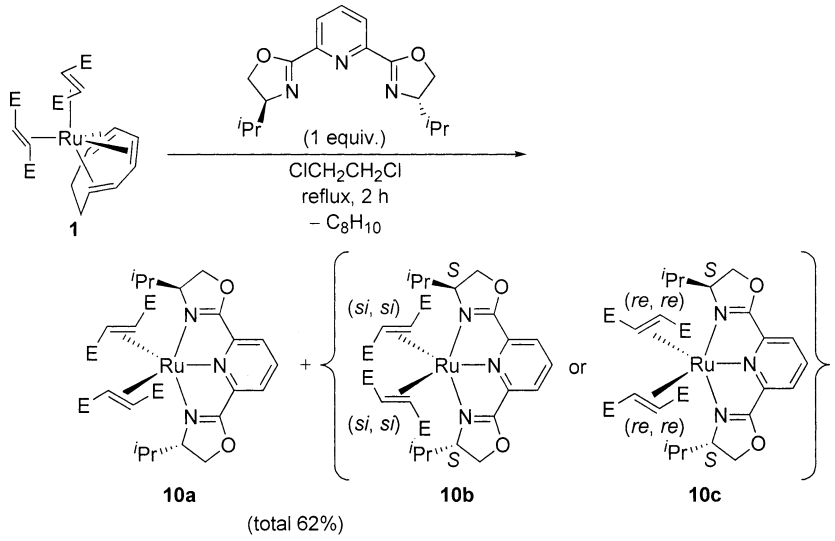
(21) (a) Motoyama, Y.; Kurihara, O.; Murata, K.; Aoki, K.; Nishiyama, H. *Organometallics* **2000**, *19*, 1025. (b) Motoyama, Y.; Murata, K.; Kurihara, O.; Naitoh, T.; Aoki, K.; Nishiyama, H. *Organometallics* **1998**, *17*, 1251.

(22) Nishiyama, H.; Naitoh, T.; Motoyama, Y.; Aoki, K. *Chem. Eur. J.* **1999**, *5*, 3509.

Scheme 2. Mechanism of the Formation of a Tridentate Nitrogen Complex



Scheme 3. Reaction of 1 with *i*-Pr-Pybox



confirmed by X-ray analysis. The used single crystals of **10a** were obtained by the recrystallization of the mixture of **10a** and **10b** (or **10c**) from acetone/pentane. The ORTEP drawing of **10a** is shown in Figure 3. The crystal data and the details are given in Table 1. The selected bond distances and angles of complex **10a** are given in Tables 2 and 3, respectively. The coordination number of **10a** is five, and it is also a zerovalent ruthenium complex satisfying the 18-electron rule. The structure of **10a** is represented by a trigonal bipyramid. The nitrogen atoms of the oxazolinyl group occupy axial positions, and the pyridyl moiety of *i*-Pr-Pybox and two dmfm ligands are coordinated at equatorial positions. One of the dmfm ligands coordinates to the ruthenium center with the (*si*, *si*) face and the other with the (*re*, *re*) face. Thus, any atoms in **10a** could not be equivalent with each other in the NMR spectra.

Unfortunately, it could not be elucidated which isomer, **10b** or **10c**, was formed. Both **10b** and **10c** have a symmetry axis including the bond between Ru and the nitrogen atom of the central pyridyl group. Thus, the results of NMR spectra of these complexes must be very similar.

Considering the steric repulsion between *i*-Pr of Pybox and the ester groups of dmfm, complex **10c** seems to be more stable than **10b**. Nishiyama and co-workers showed that the (*S*,*S*)-Ph-Pybox-coordinated ruthenium-

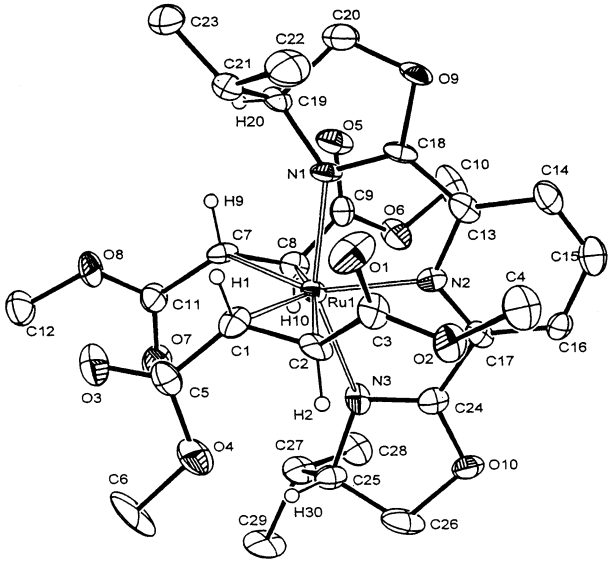


Figure 3. ORTEP drawing of Ru(dmfm)$_2$(*i*-Pr-Pybox) (**10a**). Some hydrogen atoms are omitted for clarity. Thermal ellipsoids are given at the 30% probability level.

(II) complex can select the enantioface of dmfm as the (*re*, *re*) face. This is the result of the repulsion between Ph of Pybox and the ester groups of dmfm. Thus, it could be possible to say that **10c** is more stable than the other isomers.

The mechanism for the formation of complexes **10** could also be inferred as shown in Scheme 2. This mechanism can explain the prevention of the formation of one isomer, **10b** or **10c**. The starting material **1** has two dimethyl fumarate ligands; one of which would not dissociate during the formation reaction of **10**, whereas the other would dissociate once and then re-coordinate to the ruthenium center. The enantioface of the former dmfm ligand can be either (*si*, *si*) or (*re*, *re*). On the other hand, the enantioface of the latter dmfm ligand would be selected by the (*S*,*S*)-*i*-Pr-Pybox ligand when it re-coordinates to the ruthenium center. On the basis of the results reported by Nishiyama et al.,[21] it seems likely that the (*S*,*S*)-*i*-Pr-Pybox ligand would select the enantioface of the re-coordinated dmfm ligand as (*re*, *re*). If the same selection of the enantioface is performed in the formation of **10**, the formation of **10b** might be difficult.

As for complexes **10**, the substitution of the coordinated dimethyl fumarate ligands with external dimethyl fumarate was examined. A solution of complexes **10** and $H_3CO_2CCD{=}CDCO_2CH_3$ (dimethyl fumarate-d_2; 8 equiv) in 1,2-dichloroethane was refluxed for 2 h. After solvent was evaporated, the ^{1}H NMR of the residue in $CDCl_3$ proved that none of dimethyl fumarate-d_2 was incorporated in complexes **10**. This result indicates that the dissociation and re-coordination of the dimethyl fumarate ligands do not occur, and thus there is no equilibrium between complexes **10a** and **10c** (or **10b**).

In conclusion, complex **1** is revealed to be a parent complex for various zerovalent ruthenium complexes. In contrast to the reaction of **1** with mono- or bidentate nitrogen ligands, in the present reaction with tridentate pyridyl ligands, the cot ligand of **1** was dissociated completely to afford a novel series of zerovalent complexes Ru(dmfm)$_2$(N-N′-N). Complexes **4**, **5**, **6**, **7**, and **10** are interesting complexes possessing both electron-deficient olefinic ligands and electron-rich σ-donor N-ligands. Some of the zerovalent complexes are expected to be valuable catalyst precursors.

Experimental Section

Materials and Methods. All manipulations were performed under an argon atmosphere using standard Schlenk techniques. All solvents were distilled under argon over appropriate drying reagents (sodium, calcium chloride, and calcium hydride). Complex **1**,[16] 2,6-bis(1-isopropyliminoethyl)pyridine,[7] 2,6-bis(1-phenyliminoethyl)pyridine,[7] and $H_3CO_2CCD{=}CDCO_2CH_3$ (dimethyl fumarate-d_2)[23] were synthesized as described in the literature. 2,2′:6′,2″-Terpyridine (terpy) and 2,6-bis[(4*S*)-(−)-isopropyl-2-oxazolin-2-yl]pyridine (*i*-Pr-Pybox) were obtained commercially and used without further purification. All new compounds are characterized below.

Physical and Analytical Measurements. NMR spectra were recorded on a JEOL EX-400 (FT, 400 MHz (^{1}H), 100 MHz (^{13}C)) instrument. Chemical shifts (δ) for ^{1}H and ^{13}C are referenced to internal solvent resonances and reported relative to $SiMe_4$. IR spectra were recorded using a Nicolet Impact 410 FT-IR spectrometer. HR-MS spectra were recorded on JEOL SX102A spectrometers with *m*-nitrobenzyl alcohol (*m*-NBA) as a matrix. Elemental analyses of the complexes except for **6** were performed at the Microanalytical Center of Kyoto University. Elemental analysis of **6** was performed using a Perkin-Elmer PE 2400 series II CHNS/O analyzer.

Synthesis of Ru(dmfm)$_2$(pyridine)$_3$ (4). In a 20 mL two-necked flask equipped with a reflux condenser and a stirring bar, Ru(η^6-cot)(dmfm)$_2$ (**1**; 0.50 g, 1.0 mmol) was placed under an argon atmosphere. Then 5.0 mL of pyridine was added, and the mixture was refluxed for 2 h. The solution was chromatographed on alumina (activity II−III). Elution with hexane/pyridine (50:50) gave an orange solution, from which the solvent was evaporated. The orange residue was recrystallized from CH_2Cl_2/pentane to give complex **4**·CH_2Cl_2 (0.416 g, 58% yield). Complex **4** is unstable in air even in microcrystals.

Complex 4·CH_2Cl_2: orange crystals, mp 100−102 °C dec. IR (KBr disk): 3047, 2943, 1697, 1659, 1435, 1262, 1169, 1041 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.23 (d, 2H, J = 4.8 Hz, Py), 8.11 (br, 1H, Py), 8.00 (d, 2H, J = 6.1 Hz, Py) 7.80 (t, 1H, J = 7.3 Hz, Py), 7.39 (t, 1H, J = 7.3 Hz, Py), 7.33 (t, 2H, J = 7.3 Hz, Py), 7.28 (t, 1H, J = 7.3 Hz, Py), 7.20, (br, 1H, Py), 7.09 (br, 1H, Py), 6.73 (t, 2H, J = 7.3 Hz, Py), 6.58 (br, 1H, Py), 4.23 (d, 2H, J = 8.6 Hz, =CH), 3.97 (d, 2H, J = 8.6 Hz, =CH), 3.36 (s, 6H, OMe), 2.98 (s, 6H, OMe). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 180.0 (C=O), 177.5 (C=O), 157.9 (Py), 155.6 (Py), 134.6 (Py), 134.6 (Py), 125.7 (Py), 123.2 (Py), 52.3 (=CH), 50.7 (OMe), 49.9 (OMe), 48.5 (=CH). Anal. Calcd for $C_{27}H_{31}N_3O_8Ru{\cdot}CH_2Cl_2$: C, 47.26; H, 4.67; N, 5.91; Cl, 9.96. Found: C, 46.99; H, 4.68; N, 5.83; Cl, 9.99.

Synthesis of Ru(dmfm)$_2$(terpy) (5a and 5b). In a 20 mL two-necked flask equipped with a reflux condenser and a stirring bar, Ru(η^6-cot)(dmfm)$_2$ (**1**; 1.0 g, 2.0 mmol) and terpy (0.49 g, 2.1 mmol) were placed under an argon atmosphere. Acetone (15 mL) was added, and the mixture was refluxed with stirring for 2 h. The solution was chromatographed on alumina. Elution with $CHCl_3$ gave a dark purple solution, from which the solvent was evaporated. The dark purple residue was recrystallized from acetone/pentane, and the formed microcrystals were dried under vacuum to give a mixture of complexes **5a** and **5b** (0.45 g, 36% yield). Microcrystals of **5** can be treated in air at least for several hours.

Mixture of 5a and 5b: dark purple crystals, mp 162−164 °C dec. IR spectrum (KBr disk): 2956, 1670, 1446, 1301, 1260, 1148, 1038 cm^{-1}. Anal. Calcd for $C_{27}H_{27}N_3O_8Ru$: C, 52.09; H, 4.37; N, 6.75. Found: C, 52.52; H, 4.62; N, 6.49.

Complex 5a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12−7.17 (11H, H_{Py}), 3.97 (d, 2H, J = 12.2 Hz, =CH), 3.78 (s, 6H, OMe), 3.57 (d, 2H, J = 12.2 Hz, =CH), 2.71 (s, 6H, OMe); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6 (C=O), 174.1 (C=O), 157.6 (Py), 156.7 (Py), 155.8 (Py), 155.6 (Py), 155.2 (Py), 155.2 (Py), 136.3 (Py), 135.5 (Py), 132.9 (Py), 125.5 (Py), 125.4 (Py), 121.0 (Py), 120.6 (Py), 120.0 (Py), 119.6 (Py), 52.6 (=CH), 50.8 (OMe), 49.8 (OMe), 42.9 (=CH).

Complex 5b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12−7.17 (11H, H_{Py}), 3.85 (s, 6H, OMe), 3.76 (d, 2H, J = 9.3 Hz, =CH), 3.60 (d, 2H, J = 9.3 Hz, =CH), 2.71 (s, 6H, OMe); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6 (C=O), 174.1 (C=O), 157.4 (Py), 156.5 (Py), 154.6 (Py), 135.9 (Py), 134.8 (Py), 125.6 (Py), 121.4 (Py), 119.8 (Py), 50.7 (OMe), 50.6 (=CH), 49.8 (OMe), 42.5 (=CH).

Synthesis of Ru(dmfm)$_2$[2,6-bis(1-phenyliminoethyl)pyridine] (6a and 6b). In a 20 mL two-necked flask equipped with a reflux condenser and a stirring bar, Ru(η^6-cot)(dmfm)$_2$ (**1**; 0.98 g, 2.0 mmol) and 2,6-bis(1-phenyliminoethyl)pyridine (0.62 g, 2.0 mmol) were placed under an argon atmosphere. Then 1,4-dioxane was added, and the mixture was refluxed with stirring for 2 h. The solution was chromatographed on alumina. Elution with $CHCl_3$ gave a dark purple solution, from which the solvent was evaporated. The dark purple residue was recrystallized from $CHCl_3$/pentane to give

(23) Richards, E. M.; Tebby, J. C.; Ward, R. S.; Williams, D. H. *J. Chem. Soc. C* **1969**, 1542.

a mixture of complexes **6a** and **6b** (0.29 g, 21% yield). Microcrystals of **6** can be treated in air at least for several hours.

Mixture of 6a and 6b: dark purple crystals, mp 178−181 °C dec. HR-MS FAB$^+$ (*m*/*z*): 704.1522 ([M + H]$^+$, calcd 704.1546); IR spectrum (KBr disk) 2951, 1686, 1438, 1280, 1142, 1055 cm^{-1}. Anal. Calcd for $C_{33}H_{35}N_3O_8Ru$: C, 56.40; H, 5.02; N, 5.98. Found: C, 56.59; H, 5.45; N, 6.03.

Complex 6a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02−7.88 (3H, H_{Py}), 7.40−6.98 (10H, H_{Ar}), 4.27 (d, 2H, J = 10.3 Hz, =CH), 4.14 (d, 2H, J = 10.3 Hz, =CH), 3.08 (s, 6H, OMe), 2.86 (s, 6H, OMe), 2.35 (s, 3H, Me), 1.98 (s, 3H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2 (C=O), 174.0 (C=N), 171.1 (C=O), 165.0 (C=N), 159.1 (Py), 152.7 (Py), 148.5 (Py), 148.3 (Py), 131.4 (Py), 127.9 (Ar), 127.4 (Ar), 125.7 (Ar), 125.4 (Ar), 123.9 (Ar), 122.9 (Ar), 122.7 (Ar), 122.4 (Ar), 54.0 (=CH), 49.5 (OMe), 49.3 (OMe), 46.1 (=CH), 18.7 (Me), 18.1 (Me).

Complex 6b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02−7.88 (3H, H_{Py}), 7.40−7.15 (10H, H_{Ar}), 4.21 (d, 2H, J = 10.7 Hz, =CH), 3.72 (d, 2H, J = 10.7 Hz, =CH), 3.01 (s, 6H, OMe), 2.99 (s, 6H, OMe), 2.17 (s, 6H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8 (C=O), 171.4 (C=O), 169.5 (C=N), 155.9 (Py), 148.8 (Py), 132.7 (Py), 127.6 (Ar), 125.3 (Ar), 122.9 (Ar), 122.4 (Ar), 51.3 (=CH), 49.5 (OMe), 49.3 (OMe), 47.8 (=CH), 18.7 (Me).

Synthesis of Ru(dmfm)$_2$[2,6-bis(1-isopropyliminoethyl)pyridine] (7a and 7b). In a 20 mL two-necked flask equipped with a reflux condenser and a stirring bar, Ru(η^6-cot)(dmfm)$_2$ (**1**; 0.15 g, 0.30 mmol) and 2,6-bis(1-isopropyliminoethyl)pyridine (0.084 g, 0.34 mmol) were placed under an argon atmosphere. Then 1,4-dioxane was added, and the mixture was refluxed with stirring for 2 h. The solution was chromatographed on alumina. Elution with $CHCl_3$ gave a dark purple solution, from which the solvent was evaporated. The dark purple residue was recrystallized from $CHCl_3$/pentane to give a mixture of complexes **7a** and **7b** (0.086 g, 29% yield). Microcrystals of **7** can be treated in air at least for several hours.

Mixture of 7a and 7b: dark purple crystals, mp 204−206 °C dec. IR spectrum (KBr disk): 2980, 2945, 1693, 1683, 1589, 1578, 1459, 1434 cm^{-1}. Anal. Calcd for $C_{27}H_{39}N_3O_8Ru$: C, 51.09; H, 6.19; N, 6.62. Found: C, 50.65; H, 5.97; N, 6.55.

Complex 7a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80−7.65 (3H, H_{Py}), 4.70 (heptet, 1H, J = 6.8 Hz, CH of *i*-Pr), 4.16 (d, 2H, J = 9.6 Hz, =CH), 3.97 (d, 2H, J = 9.6 Hz, =CH), 3.73 (s, 6H, OMe), 3.33 (heptet, 1H, J = 6.8 Hz, CH of *i*-Pr), 2.74 (s, 6H, OMe), 2.67 (s, 3H, Me), 2.42 (s, 3H, Me), 1.48 (d, 6H, J = 6.8 Hz, Me of *i*-Pr), 1.41 (d, 6H, J = 6.8 Hz, Me of *i*-Pr); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7 (C=O), 171.4 (C=O), 170.0 (C=N), 160.8 (C=N), 160.7 (Py), 155.9 (Py), 130.9 (Py), 122.0 (Py), 120.2 (Py), 61.9 (*i*-Pr), 57.9 (*i*-Pr), 53.6 (=CH), 50.4 (OMe), 49.6 (OMe), 43.7 (=CH), 23.0 (Me of *i*-Pr), 22.3 (Me of *i*-Pr), 19.5 (Me), 19.4 (Me).

Complex 7b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80−7.65 (3H, H_{Py}), 4.22 (d, 2H, J = 9.6 Hz, =CH), 3.97 (d, 2H, J = 9.6 Hz, =CH), 3.85 (m, 2H, J = 7.2 Hz, CH of *i*-Pr), 3.77 (s, 6H, OMe), 2.74 (s, 6H, OMe), 2.54 (s, 6H, Me), 1.45 (d, 6H, J = 7.2 Hz, Me of *i*-Pr), 1.41 (d, 6H, J = 7.2 Hz, Me of *i*-Pr); ^{13}C NMR (100 MHz, $CHCl_3$) δ 179.3 (C=O), 172.0 (C=O), 165.4 (C=N), 158.5 (Py), 133.2 (Py), 120.5 (Py), 60.5 (*i*-Pr), 50.7 (=CH), 50.4 (OMe), 49.6 (OMe), 42.8 (=CH), 23.7 (Me of *i*-Pr), 21.9 (Me of *i*-Pr), 19.6 (Me).

Synthesis of Ru(dmfm)$_2$(*i*-Pr-Pybox) (10a and 10b (or 10c)). In a 20 mL two-necked flask equipped with a reflux condenser and a stirring bar, Ru(η^6-cot)(dmfm)$_2$ (**1**; 0.50 g, 1.0 mmol) and *i*-Pr-Pybox (0.31 g, 1.0 mmol) were placed under an argon atmosphere. Then 1,2-dichloroethane was added, and the mixture was refluxed with stirring for 2 h. The solution was chromatographed on alumina. Elution with $CHCl_3$ gave a dark green solution, from which the solvent was evaporated. The dark green residue was recrystallized from $CHCl_3$/pentane to give a mixture of complexes **10a** and **10b** or **10c** (0.43 g, 62% yield). Microcrystals of **10** can be treated in air at least for several hours.

Mixture of 10a and 10b (or 10c): dark green crystals, mp 90−92 °C dec. IR spectrum (KBr disk): 2947, 2869, 2831, 1681, 1387, 1141 cm^{-1}. Anal. Calcd $C_{29}H_{39}N_3O_{10}Ru$: C, 50.43; H, 5.69; N, 6.08. Found: C, 50.42; H, 5.71; N, 5.80.

Complex 10a: ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.85−7.71 (3H, H_{Py}), 4.59 (dd, 1H, J = 4.4 Hz, J = 8.8 Hz, OC*H*H), 4.55 (dd, 1H, J = 8.8 Hz, J = 9.6 Hz, OC*H*H), 4.49 (d, 1H, J = 10.3 Hz, =CH), 4.44 (t, 1H, J = 9.2 Hz, OC*H*H), 4.34 (d, 1H, J = 10.3 Hz, =CH), 4.18 (dd, 1H, J = 8.4 Hz, J = 12.8 Hz, OC*H*H), 3.99 (d, 1H, J = 9.8 Hz, =CH), 3.90 (m, 1H, N−CH), 3.83 (m, 1H, N−CH), 3.80 (d, 1H, J = 9.8 Hz, =CH), 3.75 (s, 3H, OMe), 3.65 (s, 3H, OMe), 2.92 (s, 3H, OMe), 2.89 (s, 3H, OMe), 2.49 (m, 2H, CH of *i*-Pr), 1.15 (d, 3H, J = 6.8 Hz, Me of *i*-Pr), 0.95 (d, 3H, J = 6.8 Hz, Me of *i*-Pr), 0.80 (d, 3H, J = 6.8 Hz, Me of *i*-Pr), 0.75 (d, 3H, J = 6.8 Hz, Me of *i*-Pr); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0 (C=O), 177.8 (C=O), 173.7 (C=O), 173.0 (C=O), 150.0 (*ipso*-Py), 149.8 (C=N), 146.5 (C=N), 146.5 (*ipso*-Py), 133.2 (Py), 122.0 (Py), 121.8 (Py), 71,7 (CH_2), 71.3 (CH_2), 69.8 (=N−CH), 67.1 (=N−CH), 55.8 (=CH), 51.7 (=CH), 50.8 (OMe), 50.3 (OMe), 49.9 (OMe), 49.8 (OMe), 42.5 (=CH), 40.1 (=CH), 26.5 (CH of *i*-Pr), 26.3 (CH of *i*-Pr), 22.4 (Me), 19.6 (Me), 16.7 (Me), 14.3 (Me).

Complex 10b or 10c: ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.85−7.71 (3H, H_{Py}), 4.52 (m, 2H, OCH*H*), 4.40 (m, 2H, OC*H*H), 4.24 (d, 2H, J = 10.3 Hz, =CH), 4.12 (d, 2H, J = 10.3 Hz, =CH), 3.49 (m, 2H, N−CH), 3.03 (s, 6H, OMe), 2.52 (m, 2H, CH of *i*-Pr), 2.04 (s, 6H, OMe), 0.83 (d, 6H, J = 6.8 Hz, Me of *i*-Pr), 0.69 (d, 6H, J = 6.8 Hz, Me of *i*-Pr); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9 (C=O), 173.5 (C=O), 161.7 (C=N), 144.4 (*ipso*-Py), 134.0 (Py), 123.0 (Py), 70.8 (CH_2), 67.7 (=N−CH), 50.7 (OMe), 49.9 (OMe), 48.8 (=CH), 42.9 (=CH), 27.3 (CH of *i*-Pr), 19.5 (Me), 14.1 (Me).

Crystallographic Study of 4 and 10a. Single crystals of **4** and **10a** were obtained by recrystallization from CH_2Cl_2/pentane and acetone/pentane, respectively. The crystal data and experimental details for **4** and **10a** are summarized in Table 1. All measurements were made on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) and a rotating anode generator. The reflection intensities were monitored by three standard reflections at every 150 measurements. No decay correction was applied. Reflection data were corrected for Lorentz and polarization effects. Azimuthal scans of several reflections indicated no need for an absorption correction. The structures were solved by direct methods using SIR92[24] for **4** and **10a**, expanded using Fourier techniques, DIRDIF99,[25] and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. All hydrogen atoms in **4** and **10a** were refined using the riding model. The calculations were performed using the program system CrystalStructure crystallographic software package. The final atomic parameters for non-hydrogen atoms of **4** and **10a** are given in the Supporting Information.

Crystallographic Study of 5b. Single crystals of **5b** were obtained by recrystallization from acetone/pentane. The crystal data and experimental details for **5b** are summarized in Table 1. All measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The structures were solved by direct methods using SIR97,[26] expanded using Fourier techniques,

(24) SIR92: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(25) DIRDIF99: Beuskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-99 program system*, Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1999.

(26) SIR97: Altomare, A.; Burla, M. C.; Camali, M.; Cascarano, G. L.; Giacovazzo, C.; Gualiardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

DIRDIF94,[27] and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. All hydrogen atoms were included but not refined. The calculations were performed using the program system teXsan crystallographic software package of Molecular Structure Corporation. The final atomic parameters for non-hydrogen atoms of **5b** are given in the Supporting Information.

Acknowledgment. This work was supported in part by a Grant-in-Aid from the Japan Society for the Promotion of Science. M.S. appreciates a Research Fellowship from the Japan Society for the Promotion of Science for Young Scientists. The authors are grateful to Rigaku X-ray Research Laboratory for supporting the X-ray crystallography of **5b**.

(27) DIRDIF94: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel R.; Smits, J. M. M. *The DIRDIF-94 program system*, Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1994.

Supporting Information Available: Text giving a description of the X-ray procedures, tables of X-ray data, positional and thermal parameters, and bond lengths and angles, and ORTEP diagrams for compounds **4**, **5b**, and **10a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0208725