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Syntheses and Structures of Novel Zerovalent 2,2′-Bipyridyl or 1,10-Phenanthroline Ruthenium Complexes

Toshiaki Suzuki, Masashi Shiotsuki, 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

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Ru(1-6-η-cyclooctatriene)(η^2-dimethyl fumarate)$_2$ (**2**), which is easily derived from Ru(1-2:5-6-η-cyclooctadiene)(1-6-η-cyclooctatriene) (**1**), reacts with bidentate nitrogen ligands, 2,2′-bipyridyl or 1,10-phenanthroline, to give novel ruthenium(0) complexes, Ru(1-2:5-6-η-cyclooctatriene)(η^2-dimethyl fumarate)($N\frown N$) ($N\frown N$ = 2,2′-bipyridyl (**3a**) or 1,10-phenanthroline (**3b**)) quantitatively. On the other hand, the complex **1** reacts with dimethyl fumarate in the presence of $N\frown N$ to give novel ruthenium(0) complexes, Ru(1-2:5-6-η-cyclooctadiene)(η^2-dimethyl fumarate)($N\frown N$) ($N\frown N$ = 2,2′-bipyridyl (**4a**) or 1,10-phenanthroline (**4b**)), in high yields. The structures of the complexes **3a**, **3b,** and **4b** were established by X-ray analyses, and the coordination geometry around the central ruthenium atom in these complexes was a distorted trigonal bipyramid. The two nitrogen atoms occupy an axial and an equatorial position, respectively, the two olefinic moieties of the cyclooctatriene or cyclooctadiene occupy an axial and an equatorial position, respectively, and the dimethyl fumarate was coordinated in the equatorial plane.

Introduction

Transition metal complexes containing electron-rich ligands have been the focus of recent studies in the field of organometallic chemistry of group 8 metals.[1−10] These metal complexes are known to be stable in high formal oxidation states. Very strong σ-donor ligands 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen) have been extensively used in the coordination chemistry of ruthenium.[1−5] These ligands have been applied in homogeneous catalysis either as reducible "electron reservoirs" in metal complexes or as promoters of

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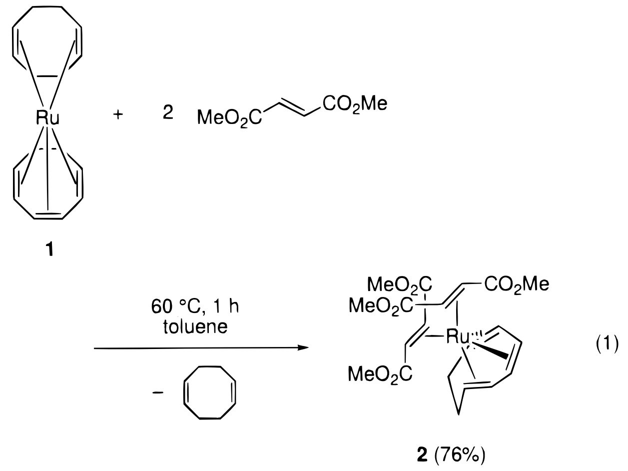
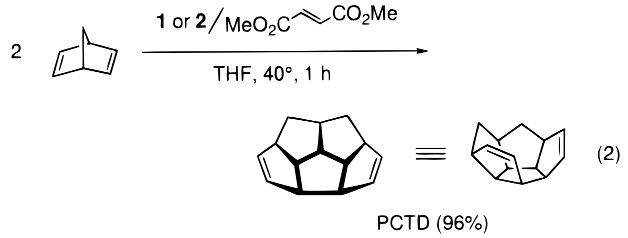
catalytic reactions.[6−10] Many Ru(II) complexes with bidentate pyridyl ligands such as 2,2′-bipyridyl or 1,10-phenanthroline have been reported, and much attention has been focused on the photo- and electrochemistry of these complexes.[2] On the other hand, only a few zerovalent ruthenium complexes with bidentate pyridyl ligands have been reported.[8−11] It has been reported that Ru(bipy)$_2$(CO)(CO$_2$), Ru(bipy)(terpy)(CO$_2$) (terpy = 2,2′:6′,2″-terpyridine), Ru(bipy)$_2$(CO)$_2$, Ru(bipy)(terpy)(CO), Ru(bipy)$_2$(CO), or Ru(bipy)(terpy) is formed in the water gas shift reaction[8] or in the processes of electrochemical[9] or photochemical[10] reduction of CO$_2$ catalyzed by a [Ru(bipy)$_2$(CO)Cl]$^+$, [Ru(bipy)$_2$(CO)$_2$]$^{2+}$, or [Ru(bipy)(terpy)(CO)]$^{2+}$ catalyst, but these complexes have not been isolated, except Ru(bipy)$_2$(CO)(CO$_2$), the structure of which has been confirmed by X-ray analysis.[11] The complex may be recognized as six-coordinate 18-electron Ru^{II}(bipy)$_2$(CO)(η^1-CO$_2$$^{2-}$) rather than 20-electron Ru^0(bipy)$_2$(CO)(CO$_2$).[12] Thus, to our knowledge, mononuclear 18-electron Ru(0) complexes with the 2,2′-bipyridyl or the 1,10-phenanthroline ligand have so far not been isolated.

Quite recently, we found that Ru(η^6-cot)(dmfm)$_2$ (**2**; η^6-cot = 1-6-η-cyclooctatriene, dmfm = η^2-dimethyl fumarate) is formed readily by the reaction of Ru(cod)(η^6-cot) (**1**; cod = 1-2:5-6-η-1,5-cyclooctadiene) with dimethyl fumarate or dimethyl maleate (eq 1).[13] The complex **2** is the first example derived from **1** by replacement of the η^4-cyclooctadiene ligand, not the η^6-cyclooctatriene ligand, by 2 mol of an olefin. The complex **2** possesses two electron-deficient olefins and the cyclooctatriene, so it is expected to have high catalytic activities. It appears that η^6 tridentate bonding is tenuous since the Ru(0) species containing bidentate η^4-cyclooctatriene are readily formed at room temperature in the presence of CO,[14] P(OMe)$_3$,[15] and PMe$_3$.[16] The tendency for the cyclooctatriene ligand to give bidentate coordination[14−16] is of particular interest and may also play an interesting role in determining catalytic activity, at least under mild conditions, by allowing the reagent involved to gain access to the metal center. The complex **2** showed excellent catalytic activity in unusual dimerization of bicyclo[2.2.1]hepta-2,5-diene to give pentacyclo[6.6.0.^{2,6}0.^{3,13}0^{10,14}]tetradec-4,11-diene (PCTD) involving carbon−carbon bond cleavage and reconstruction of a novel carbon skeleton under very mild conditions (eq 2).[13] In the course of our study on the reactivities and the catalytic activities of **1** and **2**, we found a series of novel complexes with bidentate bis(pyridyl) ligands. We report here the syntheses and the structures of novel zerovalent ruthenium complexes with bidentate bis(pyridyl) ligands derived from **1** and **2**.



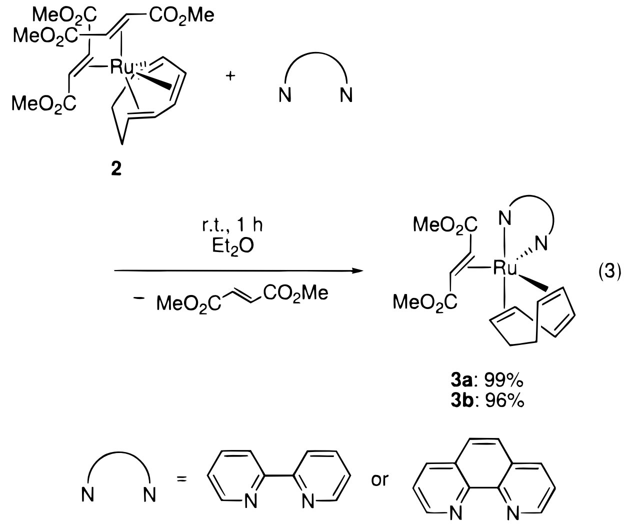
(1)



(2)

Results and Discussion

Ru(η^4-cot)(dmfm)(N⌒N) (3). Ru(η^6-cot)(dmfm)$_2$ (**2**) readily reacted with 2,2′-bipyridyl in diethyl ether at room temperature to give orange crystals of Ru(η^4-cot)(dmfm)(bipy) (**3a**, η^4-cot = 1-2:5-6-η-cyclooctatriene) in quantitative yield (eq 3). The complex **3a** is the first example of a mononuclear zerovalent ruthenium complex coordinated by bidentate pyridyl ligands. A significant feature of the complex **3a** is that it possesses both the electron-donating (bipy) and the electron-withdrawing (dmfm) ligands. Similarly, **2** readily reacted with 1,10-phenanthroline to give orange crystals of Ru(η^4-cot)(dmfm)(phen) (**3b**) quantitatively. Complex **3a** and **3b** are stable in air for 24 h. The structures of **3a** and



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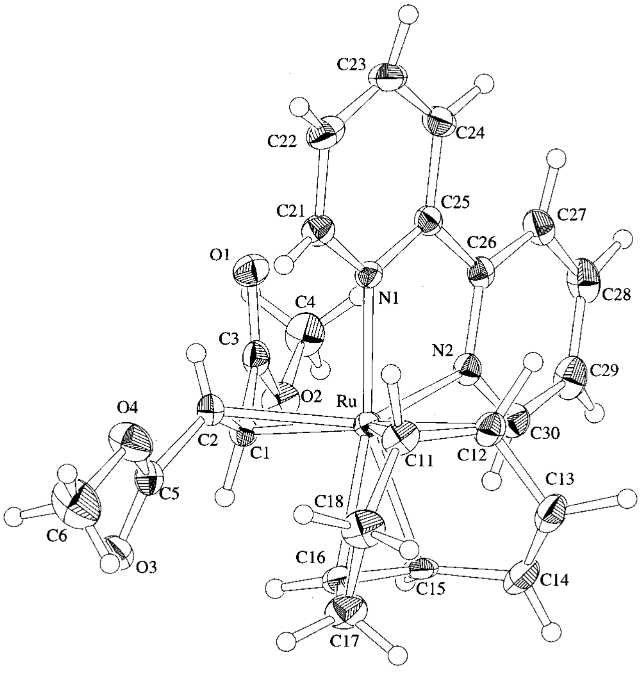

Figure 1. ORTEP drawing of the structure of **3a**. Thermal ellipsoids are shown at the 30% probability level.

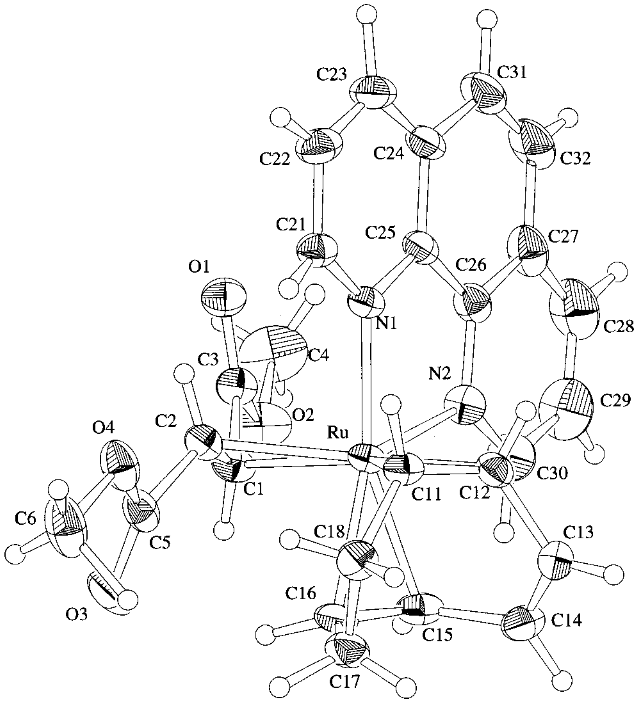

Figure 2. ORTEP drawing of the structure of **3b**. Thermal ellipsoids are shown at the 30% probability level.

3b were deduced on the basis of ^{1}H and ^{13}C NMR and IR spectra and exactly confirmed by X-ray analyses.

The structures of **3a** and **3b** are shown in Figures 1 and 2, and crystal data and the details of data collection of **3a** and **3b** are given in Table 1. Both structures are represented by a distorted trigonal bipyramid. One nitrogen and one carbon−carbon double bond of the cyclooctatriene (C(15)−C(16)) occupy two axial positions, and the other nitrogen, one carbon−carbon double bond of the cyclooctatriene (C(11)−C(12)), and the C=C bond of the dimethyl fumarate occupy the equatorial positions; the central double bond of the cyclooctatriene in **3** (C(13)−C(14)), which had been coordinated to Ru in **2**, is dissociated in **3**. The molecule does not have a symmetry plane. A few ruthenium complexes having an η^4-cyclooctatriene ligand have been reported.[14−16] Only Ru(cod)(1-4-η-1,3,5-cyclooctatriene){P(OMe)$_3$}[15] was confirmed by X-ray analysis. The structures of Ru(cod)(1-2:5-6-η-1,3,5-cyclooctatriene)(CO),[14] which was suggested to have a 1-4-η bonding mode,[15] and Ru(cod)(1-4-η-1,3,5-cyclooctatriene)(PMe$_3$)[16] were not fully established. Thus, the complexes **3a** and **3b** are, to our knowledge, the first examples of the ruthenium complexes with the 1-2:5-6-η-1,3,5-cyclooctatriene ligand whose structure is established by X-ray analysis.

Lists of the selected bond distances and bond angles of **3a** and **3b** are provided in Table 2 and Table 3, respectively. The distances between ruthenium and the axial nitrogen, Ru−N(1), are 2.084(5) Å for **3a** and 2.096(3) Å for **3b**, and they are in agreement with values observed for the Ru−N(imine) σ-bond in Ru(CO)$_2$-(dmfm)(*i*PrN=CHCH=N*i*Pr)[17] and for the Ru−N(pyridine) σ-bond in [Cp*Ru(η^2-dimethyl maleate)(bipy)]$^+$ (Cp* = pentamethylcyclopentadienyl).[18] The distances between ruthenium and the equatorial nitrogen, Ru−N(2) (2.178(5) Å for **3a** and 2.194(3) Å for **3b**), are longer than Ru−N(1), due to steric interaction with the cyclooctatriene ligand or the decrease of electron density in the Ru atom by the dimethyl fumarate ligand in equatorial position. The Ru−C(1) (2.185(6) Å for **3a** and 2.184(4) Å for **3b**) is slightly longer than Ru−C(2) (2.165(6) Å for **3a** and 2.164(4) Å for **3b**) bonds, pointing to a slightly unsymmetrical coordination of olefinic ligands.[17] This feature is probably related to their relative position with respect to the σ-donating nitrogen atom N(2) and the cyclooctatriene ligand. The distances between ruthenium and the axial olefinic carbons of the cyclooctatriene ligands, Ru−C(15) and Ru−C(16), are 2.184(6) and 2.212(6) Å for **3a** and 2.177(4) and 2.201(4) Å for **3b** and are longer than those between ruthenium and the equatorial olefinic carbons of the cyclooctatriene ligands, Ru−C(11) and Ru−C(12) (2.153(6) and 2.169(6) Å for **3a** and 2.145(4) and 2.159(4) Å for **3b**). However, all of these bond lengths are shorter than those in the complex **2** (between 2.229(6) and 2.285(6) Å)[13] due to the influence of the σ-donor nitrogen ligand.

The angles of N(1)−Ru−Ctr(15−16), where Ctr(15−16) is the center of C(15) and C(16), are 171.7° for **3a** and 173.6° for **3b**, which implies that the coordinated N(1) of the σ-donor ligand and C(15)−C(16) of the cyclooctatriene occupy the axial position. The plane through the five-membered heterometallacycle Ru−N(1)−C(25)−C(26)−N(2) is almost perpendicular to the plane defined by Ru−C(1)−C(2) (99.22° for **3a** and 95.81° for **3b**) and that defined by Ru−C(11)−C(12) (85.43° for **3a** and 90.60° for **3b**), which implies that the coordinated dimethyl fumarate and C(11)−C(12) of the cyclooctatriene lie in the equatorial plane. The largest deviations from the trigonal bipyramidal geometry are observed for the N(1)−Ru−N(2) (75.8° for **3a** and 76.6° for **3b**), indicating that the N(2) atom is slightly bent

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Table 1. Summary of Crystal Data, Collection Data, and Refinement of 3a, 3b, and 4b

	3a	**3b**	**4b**
formula	$C_{24}H_{26}N_2O_4Ru$	$C_{24}H_{26}N_2O_4Ru$	$C_{24}H_{26}N_2O_4Ru$
fw	507.55	531.57	533.59
crystal color	orange	orange	red
habit	prismatic	prismatic	prismatic
crystal size, mm	0.20 × 0.10 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.10 × 0.10
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/n$	$P2_1/c$
a, Å	15.523(9)	12.990(9)	8.516(9)
b, Å	8.295(6)	12.720(13)	11.660(10)
c, Å	16.939(6)	14.202(7)	22.964(8)
β, deg	101.40(3)	102.71(2)	93.99(6)
V, Å^3	2137(1)	2289(2)	2275(2)
Z	4	4	4
D (calcd), g cm^{-3}	1.577	1.542	1.557
data collection temp, °C	23.0	23.0	23.0
μ (Mo Kα), cm^{-1}	7.68	7.21	7.25
scan mode	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
scan speed, deg min^{-1}	8.0	8.0	8.0
scan width, deg	$1.42 + 0.30 \tan\theta$	$1.73 + 0.30 \tan\theta$	$1.47 + 0.30 \tan\theta$
$2\theta_{\max}$, deg	55.0	55.0	55.0
no. of measd reflns	5099	5476	5559
no. of obsd reflns	3722 ($I > 3.00\sigma(I)$)	3954 ($I > 3.00\sigma(I)$)	3393 ($I > 3.00\sigma(I)$)
no. of params refined	307	402	410
R,[a] %	5.1	3.3	3.6
R_w,[a] %	6.1	3.6	3.9
GOF	1.94	1.56	0.79

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o2]^{1/2}$.

Table 2. Selected Bond Distances (Å) for 3a, 3b, and 4b

	3a	**3b**	**4b**
Ru−N(1)	2.084(5)	2.096(3)	2.085(4)
Ru−N(2)	2.178(5)	2.194(3)	2.204(4)
Ru−C(1)	2.185(6)	2.184(4)	2.183(5)
Ru−C(2)	2.165(6)	2.164(4)	2.174(5)
Ru−C(11)	2.153(6)	2.145(4)	2.136(5)
Ru−C(12)	2.169(6)	2.159(4)	2.159(5)
Ru−C(15)	2.184(6)	2.177(4)	2.180(4)
Ru−C(16)	2.212(6)	2.201(4)	2.217(5)
C(1)−C(2)	1.438(9)	1.433(5)	1.439(6)
C(11)−C(12)	1.433(9)	1.416(6)	1.418(8)
C(12)−C(13)	1.49(1)	1.490(6)	1.525(8)
C(13)−C(14)	1.31(1)	1.315(6)	1.523(9)
C(14)−C(15)	1.52(1)	1.483(6)	1.517(7)
C(15)−C(16)	1.385(9)	1.407(6)	1.387(7)
C(16)−C(17)	1.525(9)	1.519(6)	1.526(8)
C(17)−C(18)	1.50(1)	1.520(6)	1.510(9)
C(18)−C(11)	1.512(10)	1.515(5)	1.510(8)

Table 3. Selected Bond Angles (deg) for 3a, 3b, and 4b[a]

	3a	**3b**	**4b**
N(1)−Ru−N(2)	75.8(2)	76.6(1)	76.8(1)
N(1)−Ru−C(1)	98.4(2)	95.9(1)	95.7(2)
N(1)−Ru−C(2)	85.6(2)	83.9(1)	85.6(2)
N(1)−Ru−C(11)	86.6(2)	87.3(1)	86.9(2)
N(1)−Ru−C(12)	86.0(2)	90.2(1)	88.8(2)
N(1)−Ru−C(15)	159.1(2)	160.3(1)	158.8(2)
N(1)−Ru−C(16)	160.7(2)	160.2(1)	161.6(2)
N(2)−Ru−C(1)	94.2(2)	92.9(1)	90.4(2)
N(2)−Ru−C(2)	125.9(2)	125.0(1)	123.9(2)
N(2)−Ru−C(11)	124.8(2)	127.3(1)	129.4(2)
N(2)−Ru−C(12)	87.5(2)	91.1(1)	92.9(2)
N(2)−Ru−C(15)	87.2(2)	86.6(2)	85.6(2)
N(2)−Ru−C(16)	123.1(2)	123.2(1)	121.4(2)
C(1)−Ru−C(2)	38.6(2)	38.5(1)	38.6(2)
C(1)−Ru−C(11)	140.4(3)	139.0(2)	139.2(2)
C(1)−Ru−C(12)	175.5(2)	173.3(1)	174.9(2)
C(1)−Ru−C(15)	94.8(2)	95.2(2)	96.2(2)
C(1)−Ru−C(16)	84.8(2)	85.2(2)	87.6(2)
C(2)−Ru−C(11)	103.6(3)	102.0(1)	101.6(2)
C(2)−Ru−C(12)	141.9(3)	140.4(1)	140.0(2)
C(2)−Ru−C(15)	114.5(2)	114.6(2)	114.4(2)
C(2)−Ru−C(16)	85.2(2)	84.8(2)	85.9(2)
C(11)−Ru−C(12)	38.7(3)	38.4(1)	38.5(2)
C(11)−Ru−C(15)	93.5(3)	94.8(2)	95.5(2)
C(11)−Ru−C(16)	79.1(3)	79.1(1)	78.9(2)
C(12)−Ru−C(15)	81.1(3)	79.6(2)	80.3(2)
C(12)−Ru−C(16)	90.8(3)	88.1(2)	87.4(2)
C(15)−Ru−C(16)	36.7(2)	37.5(2)	36.8(2)
N(1)−Ru−Ctr(1−2)	92.1	90.0	90.7
N(1)−Ru−Ctr(11−12)	86.1	88.7	87.7
N(1)−Ru−Ctr(15−16)	171.7	173.6	172.3
N(2)−Ru−Ctr(1−2)	110.4	109.2	107.4
N(2)−Ru−Ctr(11−12)	106.2	109.3	111.2
N(2)−Ru−Ctr(15−16)	105.3	105.1	103.7
Ctr(1−2)−Ru−Ctr(11−12)	141.7	140.0	139.9
Ctr(1−2)−Ru−Ctr(15−16)	95.1	95.3	96.4
Ctr(11−12)−Ru−Ctr(15−16)	85.7	84.8	85.0

[a] Definitions: Ctr(1−2), the center of C(1) and C(2); Ctr(11−12), the center of C(11) and C(12); Ctr(15−16), the center of C(15) and C(16).

out of the equatorial plane toward N(1). This is clearly the consequence of the limited bite angle of the chelating bipy or phen ligands.

The C(1)−C(2) bond lengths (1.438(9) Å for **3a** and 1.433(5) Å for **3b**) of the coordinated dimethyl fumarate ligand, which are in agreement with the values generally observed for the C−C(olefinic carbon of fumarate or maleate ligand) bonds,[13,17−22] indicate a substantial reduction of the C−C bond order, due to back-donation by the electron-rich ruthenium atom into the antibonding alkene π^*-orbital. The ester substituents are bent away from the metal as evident from the torsion angle C(3)−C(1)−C(2)−C(5) of 145.6(6)° for **3a** and 141.7(4)°

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Table 4. ^{1}H NMR Data of the Complexes 3 and 4 (δ, ppm)[a,b]

assignment	3a	3b	4a	4b
Dimethyl Fumarate				
=CH	3.53 (d, 9.5)	3.71 (d, 9.3)	3.67 (d, 9.5)	3.81 (d, 9.3)
	1.96 (d, 9.5)	2.01 (d, 9.3)	2.35 (d, 9.5)	2.29 (d, 9.3)
Me	3.75 (s)	3.80 (s)	3.74 (s)	3.77 (s)
	2.51 (s)	2.02 (s)	2.45 (s)	1.98 (s)
1,3,5-Cyclooctatriene or 1,5-Cyclooctadiene				
H_1	3.35 (ddd, 8.8, 6.4, 1.5)	3.53 (dd, 8.8, 5.8)	3.12 (dd, 8.3, 5.4)	3.31 (dd, 8.3, 4.9)
H_2	1.45 (dd, 8.8, 2.9)	1.38 (dd, 8.8, 2.9)	1.49 (td, 8.3, 5.4)	1.49 (td, 8.3, 4.9)
H_3	5.82 (dd, 7.3, 2.9)	5.81 (dd, 7.3, 2.9)	1.73 (m, 2H)	1.74 (m)
				1.66 (m)
H_4	5.90 (dd, 7.3, 2.4)	5.98 (dd, 7.3, 2.5)	2.50 (m)	2.61 (tdd, 15.1, 9.3, 5.4)
			2.34 (m)	2.38 (br dd, 15.1, 5.4)
H_5	3.50 (dd, 8.3, 2.4)	3.74 (dd, 7.8, 2.5)	3.16 (dd, 8.8, 5.4)	3.42 (dd, 8.8, 5.4)
H_6	3.10 (ddd, 8.3, 7.3, 5.4)	3.23 (td, 7.8, 5.4)	2.72 (td, 8.8, 5.4)	2.83 (td, 8.8, 5.4)
H_7	2.13 (m, 2H)	2.19 (m, 2H)	2.01 (m)	2.06 (m)
			1.73 (m)	1.71 (m)
H_8	2.67 (dddd, 13.7, 10.5, 9.8, 6.4)	2.77 (m)	2.54 (m)	2.65 (dddd, 14.7, 13.7, 8.3, 4.9)
	2.47 (m)	2.55 (dd, 12.7, 2.9)	2.42(m)	2.46 (br dd, 13.7, 8.1)
2,2′-Bipyridyl or 1,10-Phenanthroline				
	9.59 (d, 5.9)	9.87 (d, 4.9)	9.42 (d, 4.9)	9.74 (d, 5.4)
	9.07 (d, 5.9)	9.32 (d, 4.9)	9.20 (d, 5.4)	9.45 (d, 5.4)
	8.19 (d, 8.3)	8.47 (d, 8.3)	8.20 (d, 8.3)	8.44 (d, 8.3)
	8.02 (d, 8.3)	8.21 (d, 8.3)	8.02 (d, 8.3)	8.19 (d, 8.3)
	7.98 (dd, 8.3, 7.3)	7.94 (d, 8.8)	7.94 (dd, 8.3, 7.3)	7.92 (d, 8.8)
	7.72 (dd, 8.3, 7.3)	7.92 (dd, 8.3, 4.9)	7.69 (dd, 8.3, 7.3)	7.89 (dd, 8.3, 5.4)
	7.56 (dd, 7.3, 5.9)	7.90 (d, 8.8)	7.51 (dd, 7.3, 4.9)	7.89 (d, 8.8)
	7.32 (dd, 7.3, 5.9)	7.66 (dd, 8.3, 4.9)	7.31 (dd, 7.3, 5.4)	7.67 (dd, 8.3, 5.4)

[a] Measured in CD_2Cl_2 solution at room temperature and 400 MHz. [b] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Figures in parentheses are the values of the coupling constants, J_{H-H} (in Hz).

for **3b**, thus deviating 34.4(6)° and 38.3(4)°, respectively, from 180°.[13,17]

The coordinated triene moiety of the cyclooctatriene ligand is characterized by C−C bond lengths that significantly differ from each other. The C−C bond lengths of the coordinated double bonds of the cyclooctatriene on the axial position, C(15)−C(16), are 1.385(9) Å for **3a** and 1.407(6) Å for **3b** and shorter than that on the equatorial position, C(11)−C(12), which is 1.433(9) Å for **3a** and 1.416(6) Å for **3b**. The C−C bond lengths of the central double bond of the cyclooctatriene, C(13)−C(14), are 1.31(1) Å for **3a** and 1.315(6) Å for **3b**, which are shorter than the others. The shortening of the carbon−carbon double bond in **3a** and **3b** compared with free olefin (1.34 Å) is also observed in Ru(cod)(1-4-η-cot){P(OMe)$_3$}, 1.29(5) Å.[15] These phenomena are also observed in Ru(6-η:1-3-η-C_8H_{10})(PMe_3)$_3$ (1.321(8) Å),[23] in [Ru(1-5-η-C_8H_9)($C_6H_3Me_3$)]$^+$ (1.280(6) Å),[24] in [Ru(1-3:6-7-η-C_8H_9)($C_6H_3Me_3$)]$^+$ (1.28(1) Å),[24] etc.

The triene fragment of **3a** and **3b** is far from the plane; the dihedral angles of C(11)−C(12)−C(13)−C(14) are 69.4(10)° for **3a** and 73.5(6)° for **3b,** and those of C(13)−C(14)−C(15)−C(16) are −64.8(9)° for **3a** and −63.2(6)° for **3b**. The results are quite different from those in **2**,[13] which are 10(1)° and −13(1)°. The bonding patterns indicating substantial electron delocalization within the conjugated π-system are not observed for the triene moiety of **3a** and **3b**, both of which exhibit a marked C−C/C=C change in its carbon−carbon bond lengths, in contrast with Ru(η^6-cot)(dmfm)$_2$ (**2**),[13] in which the C−C bond lengths of the triene moiety are 1.407(9), 1.43(1), 1.42(1), 1.42(1), and 1.401(8) Å, respectively, and with Ru(cod)(η^6-cot) (**1**),[25] which are 1.389(9), 1.373(12), 1.415(10), 1.398(11), and 1.422(8) Å, respectively, indicating the conjugated π-system.

^{1}H and ^{13}C NMR data, summarized in Tables 4 and 5, respectively, showed that none of the protons and carbons of the cyclooctatriene are equivalent, and two doublets of doublet peaks of the noncoordinated olefinic protons are observed at δ 5.90 and 5.82 ppm for **3a** and at δ 5.98 and 5.81 ppm for **3b**; the two signals of the noncoordinated olefinic carbons appeared at δ 136.1 and 135.9 ppm for **3a** and at δ 136.6 and 136.0 ppm for **3b**. The signal at δ −0.46 ppm in the complex **2**,[26] which was assigned to one of the methylene protons of the cyclooctatriene moiety, disappeared, and one of the olefinic protons appeared in high field, δ 1.45 ppm for **3a** and δ 1.38 ppm for **3b**, due to the ring current of the pyridyl ring.

Concerning the dimethyl fumarate ligand, the two olefinic protons are not equivalent, and one of them is observed at unusual upfield (δ 1.96 ppm for **3a**, δ 2.01 ppm for **3b**). Usually, the upfield shifts of the olefinic protons of the fumarate or the maleate ligand in the ruthenium complexes appear between δ 3.1 and 4.9 ppm,[17−22] which are attributed to the increase in electron density due to π-back-bonding or which reflect a considerable degree of rehybridization (sp^2 to sp^3) of the alkene C atom. These unusual upfield shifts of the olefinic protons are also observed in Ru(CO)$_2$(η^2-dimethyl maleate)(L_1)(L_2), where L_1 and L_2 are PMe_2Ph or P(OMe)$_3$, between δ 2.10 and 2.37 ppm.[20] The two

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(26) This high-field shift of one of the methylene protons is interpreted reasonably by the magnetic anisotropy of the η^6-triene plane. In the most stable conformation of **2**, the two methylene groups in the cyclooctatriene ligand become staggered. Thus, the *endo*-proton of the methylene is located on the π-system and the signal is found at high field.[27−30]

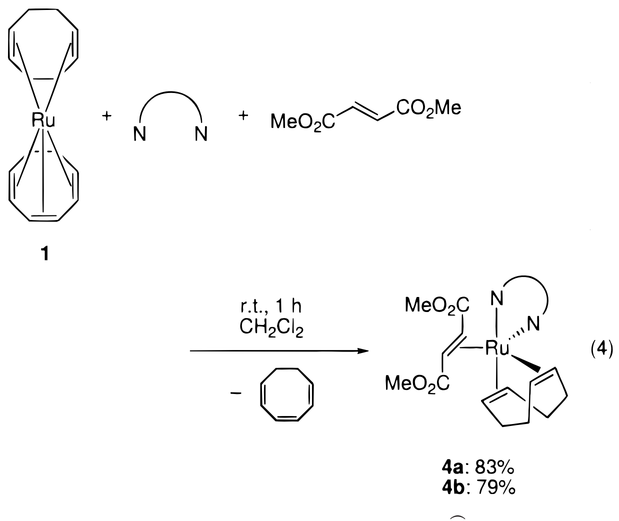
Table 5. ^{13}C NMR Data of the Complexes 3 and 4 (δ, ppm)[a,b]

assignment	**3a**	**3b**	**4a**	**4b**
	Dimethyl Fumarate			
C=O	178.0	178.3	178.1	178.3
	173.8	173.9	173.9	173.9
=CH	47.9 (151)	47.1 (151)	48.4 (151)	47.7 (151)
	44.8 (157)	44.5 (156)	43.5 (156)	43.4 (156)
Me	50.8 (145)	50.9 (145)	50.8 (145)	50.9 (145)
	49.4 (145)	48.8 (145)	49.2 (145)	48.7 (145)
	1,3,5-Cyclooctatriene or 1,5-Cyclooctadiene			
C_1	80.0 (151)	79.2 (151)	76.9 (149)	76.6 (147)
C_2	69.8 (147)	69.2 (145)	67.2 (149)	66.2 (148)
C_3	135.9 (156)	136.6 (156)	27.3 (124)	27.2 (127)
C_4	136.1 (156)	136.0 (154)	33.5 (123)	33.2 (123)
C_5	81.8 (149)	82.1 (156)	79.9 (153)	80.0 (153)
C_6	94.7 (155)	94.7 (160)	87.5 (156)	87.6 (160)
C_7	31.1 (125)	31.0 (125)	30.2 (127)	30.2 (127)
C_8	36.1 (123)	36.2 (125)	35.8 (121)	36.0 (125)
	2,2′-Bipyridyl or 1,10-Phenanthroline			
	155.1	154.9 (184)	155.1	154.3 (180)
	154.8 (182)	153.4 (184)	153.8 (184)	153.5 (184)
	154.2	146.3	153.7	146.3
	153.8 (180)	146.0	153.7 (184)	145.8
	136.4 (165)	135.5 (166)	136.2 (165)	135.3 (166)
	134.5 (166)	133.6 (166)	134.0 (166)	133.0 (166)
	124.72 (167)	129.7	124.4 (167)	130.1
	124.68 (167)	129.5	124.2 (167)	129.6
	121.6 (167)	127.4 (165)	122.1 (164)	127.5 (166)
	121.2 (164)	127.1 (165)	121.1 (164)	127.0 (166)
		124.2 (167)		124.0 (167)
		124.2 (167)		123.7 (167)

[a] Measured in CD_2Cl_2 solution at room temperature and 100 MHz. [b] Figures in parentheses are the values of the coupling constants, J_{C-H} (in Hz).

methoxy groups are not equivalent, and the signals for one of the methyl groups appear at unusually high field, δ 2.51 ppm for **3a** and δ 2.02 ppm for **3b**, due to the ring current of the pyridyl ligands.

Ru(cod)(dmfm)(N⁀N) (4). In the presence of 2,2-bipyridyl or 1,10-phenanthroline, the reaction of Ru(cod)(η^6-cot) (**1**) with 1 equiv of dimethyl fumarate in CH_2Cl_2 at room temperature generated Ru(cod)(dmfm)(N⁀N) (**4a**, N⁀N = 2,2-bipyridyl; **4b**, N⁀N = 1,10-phenanthroline) in high yields (eq 4), although the complex **1** itself does not react with N⁀N. Complexes **4a** and **4b** are stable in air for 24 h. The structures of **4a** and **4b** were characterized by ^1H and ^{13}C NMR and IR spectra, and the structure of **4b** was confirmed by X-ray analysis.



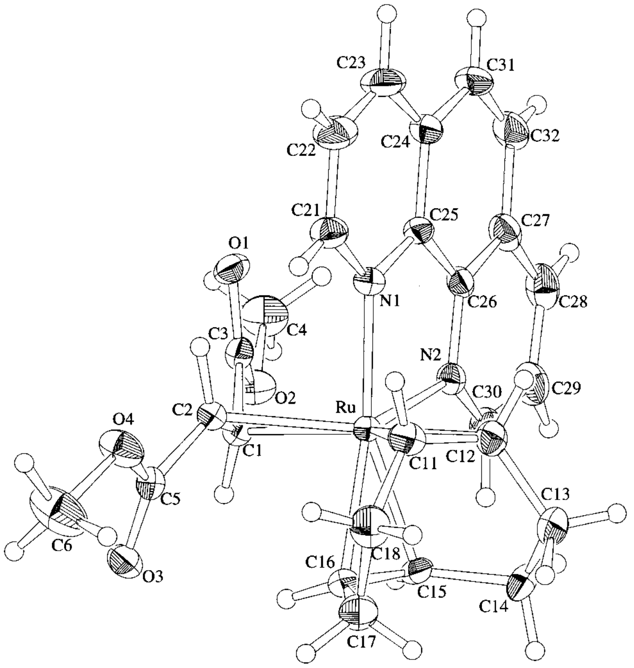


Figure 3. ORTEP drawing of the structure of **4b**. Thermal ellipsoids are shown at the 30% probability level.

The structure of **4b** is shown in Figure 3, and crystal data and the details of data collection of **4b** are also given in Table 1. Lists of selected bond distances and bond angles of **4b** are provided in Tables 2 and 3. The molecular structure of **4b** is quite similar to that of **3b**, except the coordination of the 1-2:5-6-η-cycloocta*diene* to the Ru atom instead of the 1-2:5-6-η-cycloocta*triene*.

^1H and ^{13}C NMR spectra of **4a** and **4b**, summarized in Tables 4 and 5, respectively, showed that these complexes are the analogues of **3a** and **3b**. One of the olefinic protons of the cyclooctadiene (H(12)) is shifted upfield to δ 1.49 ppm for **4a** and **4b** due to the ring current of the pyridine ring, although all the olefinic protons of the cyclooctadiene ligand in Ru(cod)(η^6-cot) (**1**) are observed between δ 2.8 and 3.0 ppm. Concerning the dimethyl fumarate ligand, the olefinic and the methyl protons are observed nonequivalently as in **3a** and **3b**.

Mechanism of the Formation of 3 and 4. A plausible mechanism of the formation of **3** and **4** is shown in Scheme 1. The reaction of **1** with 2 equiv of dimethyl fumarate in toluene gave the complex **2** irreversibly with liberation of the cyclooctadiene ligand.[13] The complex **2** would react with bidentate σ-donor ligands (N⁀N) to give Ru(η^6-cot)(dmfm)(η^1-N⁀N) (**5**) by the dissociation of the dimethyl fumarate and the coordination of one of the nitrogens of the N⁀N,[31] followed by the replacement of the central olefin of the

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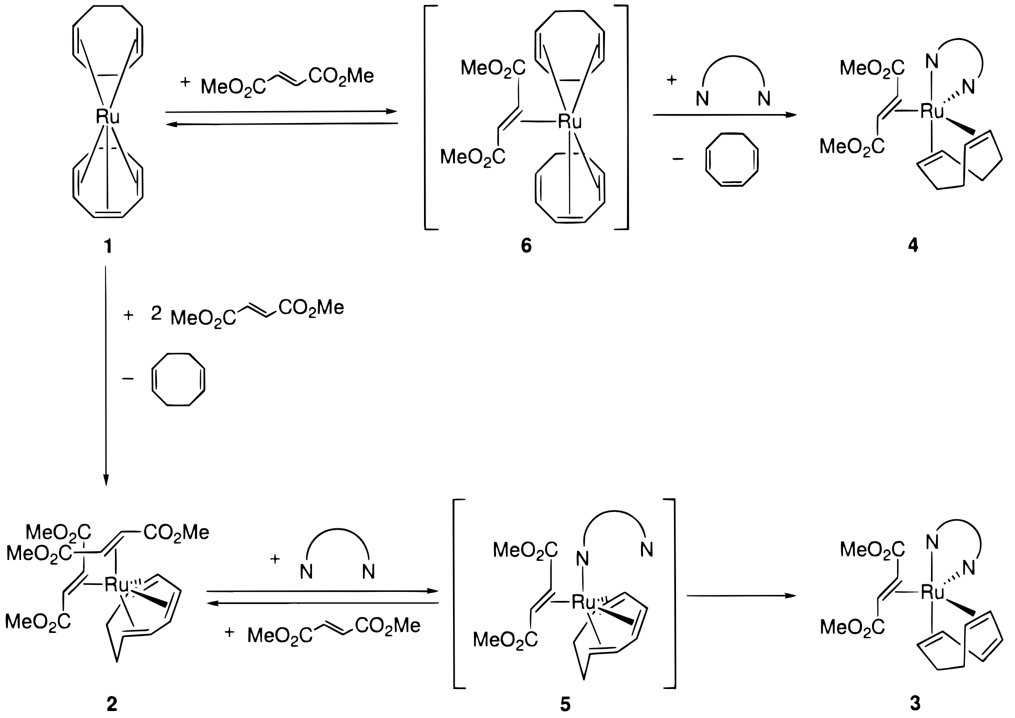
(31) The reactions of the complex **2** with tertiary monodentate phosphines (PR_3) gave the corresponding complexes, Ru(η^6-cot)(dmfm)(PR_3), which were confirmed by X-ray analyses. The results of the reaction will be reported separately.

Scheme 1. A Plausible Mechanism for the Formation of 3 and 4



cyclooctatriene with the other nitrogen moiety of the N⌒N to give Ru(η^4-cot)(dmfm)(η^2-N⌒N) (**3**).

On the other hand, complex **1** would react with 1 equiv of dimethyl fumarate to give Ru(cod)(η^4-cot)(dmfm) (**6**) reversibly. In the presence of the bidentate nitrogen ligands (N⌒N), the cyclooctatriene ligand of the intermediate **6** would be replaced by N⌒N to give Ru(cod)(dmfm)(η^2-N⌒N) (**4**).

Thus, from Ru(cod)(η^6-cot) (**1**), dimethyl fumarate and the bidentate nitrogen ligands (N⌒N), two kinds of zerovalent ruthenium complexes, the cycloocta*triene* complexes **3** and the cycloocta*diene* complexes **4,** could be synthesized in high yields.

Conclusions

The complex **2**, which cleaves carbon−carbon bonds in the dimerization of 2,5-norbornadiene, is expected to be widely used as a versatile zerovalent ruthenium complex, to provide many useful catalytic systems by the combination with suitable ligands, and to be a valuable starting material for Ru(0) complexes, as well as **1**. Furthermore, the complexes **3** and **4** were found to be interesting compounds, possessing both electron-deficient olefin and electron-rich σ-donor N-ligands, which are expected to have versatile catalytic activities.

Experimental Section

Materials and Methods. All manipulations were performed under an argon atmosphere using standard Schlenk techniques. Ru(cod)(η^6-cot)[32] and Ru(η^6-cot)(dmfm)$_2$[13] were synthesized as described in the literature. All solvents were distilled under argon over appropriate drying reagents (sodium, calcium hydride, sodium benzophenone ketyl, or calcium chloride). Dimethyl fumarate, dimethyl maleate, 2,2′-bipyridyl, and 1,10-phenanthroline 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 shift values (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. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Synthesis of Ru(η^4-cot)(dmfm)(bipy), 3a. To a suspension of 0.50 g (1.0 mmol) of Ru(η^6-cot)(dmfm)$_2$ (**2**) in 35 mL of Et$_2$O was added a solution of 0.17 g (1.1 mmol) of 2,2′-bipyridyl in 2.0 mL of Et$_2$O, and the mixture was stirred at room temperature. Orange microcrystals precipitated immediately. After 1 h, the product was separated by filtration, washed with Et$_2$O, and dried under vacuum to give **3a** (0.50 g, yield 99%). Satisfactory elemental analysis data were obtained without recrystallization.

Complex **3a**: Orange crystals, mp (dec) 214−215 °C. Anal. Calcd for $C_{24}H_{26}N_2O_4Ru$: C, 56.80; H, 5.16; N, 5.52. Found: C, 56.50; H, 5.21; N, 5.50. IR spectrum (KBr disk): 1690, 1667, 1467, 1433, 1298, 1142, 1043, 774 cm^{-1}.

Synthesis of Ru(η^4-cot)(dmfm)(phen), 3b. To a suspension of 0.50 g (1.0 mmol) of Ru(η^6-cot)(dmfm)$_2$ (**2**) in 20 mL of Et$_2$O was added a suspension of 0.20 g (1.1 mmol) of 1,10-phenanthroline in 20.0 mL of Et$_2$O, and the mixture was stirred at room temperature. Orange microcrystals precipitated immediately. After 1 h, the product was separated by filtration, washed with Et$_2$O, and dried under vacuum to give **3b** (0.51 g, yield 96%). Satisfactory elemental analysis data were obtained without recrystallization.

Complex **3b**: Orange crystals, mp (dec) 228−229 °C. Anal. Calcd for $C_{26}H_{26}N_2O_4Ru$: C, 58.75; H, 4.93; N, 5.27. Found: C, 58.55; H, 4.95; N, 5.28. IR spectrum (KBr disk): 1700, 1666, 1426, 1300, 1151, 1043, 843 cm^{-1}.

Synthesis of Ru(cod)(dmfm)(bipy), 4a. To a solution of 0.95 g (3.0 mmol) of Ru(cod)(η^6-cot) (**1**) and 0.48 g (3.1 mmol) of 2,2′-bipyridyl in 3.0 mL of CH$_2$Cl$_2$ was added a solution of 0.45 g (3.1 mmol) of dimethyl fumarate in 3.0 mL of CH$_2$Cl$_2$. The mixture was stirred at room temperature for 1 h, and the

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color of the solution changed from yellow to dark red. After the reaction mixture was concentrated in vacuo, reddish-orange microcrystals precipitated on adding pentane, and they were separated by filtration, washed with CH_2Cl_2/pentane, and dried under vacuum to give **4a** (1.27 g, yield 83%).

When the reaction was carried out in Et_2O, reddish-orange microcrystals precipitated from the reaction mixture. After 1 h, the product was separated by filtration, washed with Et_2O, and dried under vacuum to give **4a** (yield 77%), an elemental analysis of which gave satisfactory data without recrystallization.

Complex **4a**: Reddish-orange crystals, mp (dec) 192−193 °C. Anal. Calcd for $C_{24}H_{28}N_2O_4Ru$: C, 56.57; H, 5.54; N, 5.50. Found: C, 56.29; H, 5.66; N, 5.49. IR spectrum (KBr disk): 1687, 1666, 1468, 1433, 1297, 1145, 1042, 771 cm^{-1}.

Synthesis of Ru(cod)(dmfm)(phen), 4b. To a solution of 0.95 g (3.0 mmol) of Ru(cod)(η^6-cot) (**1**) and 0.51 g (3.1 mmol) of 1,10-phenanthroline in 2.0 mL of CH_2Cl_2 was added a solution of 0.45 g (3.1 mmol) of dimethyl fumarate in 2.0 mL of CH_2Cl_2. The mixture was stirred at room temperature for 1 h, the color of the solution changed from yellow to dark red, and a dark red powder precipitated. After the reaction mixture was concentrated, dark red microcrystals precipitated on adding pentane, and they were separated by filtration, washed with CH_2Cl_2/pentane, and dried under vacuum to give **4b** (1.27 g, yield 79%).

Complex **4b**: Dark red crystals, mp (dec) 226−228 °C. Anal. Calcd for $C_{26}H_{28}N_2O_4Ru$: C, 58.53; H, 5.29; N, 5.25. Found: C, 58.49; H, 5.29; N, 5.23. IR spectrum (KBr disk): 1690, 1671, 1420, 1297, 1148, 1042, 843 cm^{-1}.

Crystallographic Study of 3a, 3b, and 4b. Single crystals of complexes **3a**, **3b**, and **4b** obtained by recrystallization from CH_2Cl_2/pentane were subjected to X-ray crystallographic analyses. The crystal data and experimental details for **3a**, **3b**, and **4b** 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. Absorption corrections were empirically applied. The structures were solved by direct methods using SHELX86[33] for **3a** and SIR92[34] for **3b** and **4b**, expanded using Fourier techniques, DIRDIF94,[35] and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Atomic scattering factors and anomalous dispersion terms were taken from the literature.[36−38] Hydrogen atoms were found except for the methyl protons for **3a**, **3b**, and **4b** and hydrogens on C(13) and C(18) of **3a** and on C(17) of **4b**. Hydrogens' positions in **3a** were not refined, and isotropic *B* values were refined. Hydrogens in **3b** and **4b** were refined isotropically. The final *R* and R_w values were 0.051 and 0.061 for **3a**, 0.033 and 0.036 for **3b**, and 0.036 and 0.039 for **4b**, respectively. The calculations were performed on an IRIS Indigo and O_2 computer using the program system teXsan.[39]

The final atomic parameters for non-hydrogen atoms of **3a**, **3b**, and **4b** are given in the Supporting Information, and selected bond distances and angles are summarized in Tables 2 and 3, respectively.

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Supporting Information Available: Description of the X-ray procedures, tables of X-ray data, positional and thermal parameters, bond lengths and angles, and an ORTEP diagram for compounds **3a**, **3b**, and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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