■ Supporting Information

Isolation of *trans*-2,5-Bis(methoxycarbonyl)ruthenacyclopentane by Oxidative Coupling of Methyl Acrylate on Ruthenium(0) as an Active Intermediate for Tail-to-tail Selective Catalytic Dimerization

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Experimental

General procedures

All manipulations were carried out under dry nitrogen using standard Schlenk and vacuum line techniques. Benzene, toluene, hexane and THF were dried over anhydrous calcium chloride and then distilled from sodium wire under nitrogen with benzophenone ketyl as an indicator. Acetonitrile was dried over calcium chloride and distilled over calcium hydride under nitrogen. Ru(η^6-naphthalene)(η^4-1,5-COD) (**1**) was prepared according to the reported method.[1] Methyl acrylate was distilled under nitrogen. Deuterated solvents for use in NMR experiments were purchased from Kanto Chemical and dried with sodium wire for C_6D_6 and $C_6D_5CD_3$, and calcium hydride for CD_3CN and were directly vacuum transferred into an NMR tube. NMR spectra were recorded on a JEOL LA-300 or ECX-400 spectrometers (300.4 MHz or 399.8 MHz for ^{1}H) with chemical shifts reported in ppm downfield from TMS for ^{1}H and from 85% H_3PO_4 in D_2O for ^{31}P NMR. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer using KBr disks. GLC analysis was performed on a Shimadzu GC-14B with FID detector equipped with a capillary column (TC-1, 0.25 mmf x 30 m). $CHPh_3$ was used as an internal standard. Elemental analyses were carried out using a Perkin-Elmer 2400 series II CHN analyzer. GC-MS spectra were performed on a Shimadzu QP2010 equipped with a capillary column (TC-1, 0.25 mmf x 30 m).

Reaction of 1 with methyl acrylate. (A) Complex **1** (176.2 mg, 0.523 mmol) was placed in a 25 mL Schlenk tube, into which hexane (10 mL) was added by vacuum distillation. Methyl acrylate (200 μL, 2.22 mmol) was added to the solution by a hypodermic syringe to give immediate deposition of an off yellow powder. The mixture was stirred for 1 h at room temperature and then the reaction system was set aside at −20 ˚C for an additional hour. The yellow-brown solution was removed by cannula. The resulting solid was washed with hexane and dried under reduced pressure to give [*trans*-Ru{C^{2}H{C(O^1)OMe}C^{3}H$_2$C^{4}H$_2$C^{5}H{C(O^2)OMe}-κ^1-*C*^{2},κ^1-*O*^{1},κ^1-*C*^{5},μ-κ^1-*O*^{2}}(η^4-1,5-COD)]$_2$ (**2**) as an off-yellow powder in 67 % yield (134.5 mg, 0.177 mmol as a dimer). ^{1}H NMR (400 MHz, C_6D_6, 17.8 ˚C): δ 1.34-1.44 (m, 1H, C*H*$_2$ in COD), 1.45-1.58 (m, 1H, C*H*$_2$ in COD), 1.58-1.75 (m, 1H, C*H*$_2$ in COD), 1.79-1.91 (m, 1H,

CH_2 in COD), 2.05 (br dd, J = 13, 6 Hz, 1H, CH_2 in COD), 2.14 (br dd, J = 14, 8 Hz, 1H, CH_2 in COD), 2.27-2.40 (m, 3H, 3- and 4-CH_2 (1H), and CH_2 in COD), 2.40-2.52 (m, 3H, 3- and 4-CH_2 (1H), and CH_2 in COD), 2.68-2.79 (m, 1H, =C*H* in COD), 2.93 (m, 2H, 3- and 4-CH_2), 3.19 (overlapped with the OMe resonance, 1H, 2- or 5-C*H*CO_2Me), 3.20 (s, 3H, O*Me*), 3.35-3.40 (br m, 1H, =CH_2 in COD), 3.60 (s, 3H, O*Me*), 3.75 (br t, J = 8 Hz, 1H, 5- or 2-C*H*CO_2Me). IR (KBr, cm^{-1}): 1602 (vs, νCO).

On the other hand, the yellow-brown mother liquor of the hexane solution was characterized by GLC and after removal of all volatile matters, the residue was analyzed by the NMR spectrum. This experiment indicated that the mother liquor contained naphthalene (0.52 mmol, 100%) and dimethyl (*E*)-hexenedioate (0.98 mmol, 88% yield based on methyl acrylate, TON = 1.9).

(B) Complex **1** (15.5 mg, 0.0460 mmol) was dissolved in freshly distilled hexane (5 mL) and methyl acrylate (84 μL, 0.93 mmol, 20 equiv) was added by a hypodermic syringe. After 1 h stirring at 20 ˚C, the GLC analysis showed formation of dimethyl (*E*)-hexenedioate in 12% yield (0.056 mmol, TON = 1.2).

Treatment of 2 with acetonitrile. Complex **2** (124.9 mg, 0.3275 mmol) was recrystallized from cold acetonitrile (–30 ˚C) to give yellow crystals of bis(acetonirile)-*trans*-2,5-di(methoxycarbonyl)ruthenacyclopentane *trans*-Ru[CH(CO_2Me)CH_2CH_2C*H*CO_2Me](η^4-1,5-COD)(NCMe)$_2$ (**3**) in 35% yield (82.0 mg, 0.177 mmol). **3**: ^{1}H NMR (400 MHz, CD_3CN, 17.6 ˚C): δ 1.36-1.57 (m, 3H, CH_2 in COD), 1.69-1.81 (m, 3H, CH_2 in COD), 1.95 (s, 6H, NC*Me*), 2.08-2.18 (m, 4H, 3- and 4-CH_2, and CH_2 in COD), 2.34 (dd, J = 9.6, 6.0 Hz, 1H, =C*H* in COD), 2.51-2.65 (m, 3H, 3- and 4-CH_2, and CH_2 in COD), 2.93 (br t, J = 7 Hz, 1H, 2- or 5-C*H*CO_2Me), 3.09 (td, J = 8.7, 5.0 Hz, 1H, =CH_2 in COD), 3.20 (dd, J = 8.7, 5.5 Hz, 1H, =CH_2 in COD), 3.36 (s, 3H, O*Me*), 3.48 (s, 3H, O*Me*), 3.55 (br t, J = 7.5 Hz, 1H, 5- or 2-C*H*CO_2Me), the NCMe signal was observed at δ 1.95 (s, 6H) but this shows identical chemical shift to free NCMe. Rapid exchange between the NCMe ligands and $NCCD_3$ is considered to take place. IR (KBr, cm^{-1}): 1676 (vs, νCO), 1655 (vs, νCO). Anal.: Calcd for $C_{20}H_{30}O_4N_2$: C, 51.82; H, 6.52; N, 6.04. Found: C, 51.62; H, 6.07; N, 6.03.

Acidolysis of 2. Complex **2** (11.3 mg, 0.0296 mmol) was placed in an NMR tube into

which C_6D_6 (0.6 mL) was added by vacuum distillation. Dry hydrogen chloride gas (2.0 mL, 0.082 mmol) was added to the solution by use of mercury manometer. On the basis of an internal standard (triphenylmethane), formation of dimethyl hexanedioate was observed in 50% yield (0.015 mmol).

Acidolysis of 3. Complex **3** (12.3 mg, 0.0265 mmol) was placed in an NMR tube into which CD_3CN (0.6 mL) was added. Dry hydrogen chloride gas (2.3 mL, 0.095 mmol) was added to the solution. Formation of dimethyl hexanedioate was observed in 60% yield (0.016 mmol).

Catalytic Dimerization of Methyl Acrylate by 3. Complex **3** (37.8 mg, 0.0815 mmol) was placed in an ampoule tube into which acetonitrile (43 μL, 0.82 mmol) and methyl acrylate (75 μL, 0.83 mmol) was added. Then THF (5 mL) was transferred into the vessel by vacuum distillation and the tube was flame-sealed. The reaction system was heated at 140 ˚C for 40 min. The GLC analysis showed formation of dimethyl (*E*)-2-hexenedioate in 52% yield based on methyl acrylate.

X-ray analysis of 3. A Rigaku AFC-7R Mercury-II with graphite-monochromated Mo-*K*α (λ = 0.71069 Å) was used for data collection. A selected single crystal of **3** suitable for X-ray analysis was mounted on the top of glass capillary by use of Paraton N oil under argon. The reflection data were collected at 200 K under cold nitrogen stream. The collected data were solved by direct methods (SIR92), and refined by a full-matrix least-square procedure using SHELXL97[2] on CrystalStructure ver. 3.8 package program.[3] The crystal belonged to space group *C*2/c. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were found from the differential Fourier map and were not refined.

Preliminary X-ray analysis of 2. Crystals of **2** was obtained from cold THF. A selected crystal of **2** for X-ray analysis was mounted in a capillary tube (GLAS 0.7 mmf). The reflection data were collected at 200 K under cold nitrogen stream. The collected data were solved by direct methods (SIR92), and refined by a full-matrix least-squre procedure using SHELXL97.[2] The crystal belonged to space group *P*-1. All non-hydrogen atoms except incorporated THF were refined with anisotropic

displacement parameters and hydrogen atoms were placed in theoretical positions and were refined using a riding model.

Table S1. Physical and Crystallographic Parameters for 3.

	3
Formula	$C_{20}H_{30}N_2O_4Ru$
Formula weight	463.54
Crystal system	*monoclinic*
Space group	*C*2/c (*No.*15)
Unit cell dimensions	
a (Å)	22.828(5)
b (Å)	14.256(3)
c (Å)	15.801(4)
β (deg)	127.721(2)
V (Å^3)	4067.4(15)
Z	8
D_{calcd} (g cm^{-1})	1.514
Temp (K)	200.0
F(000)	1920.00
μ (mm^{-1})	0.798
Reflns number total	15612
No. of observed eflections [$F^2>2\sigma(F^2)$]	5697
Crystal size (mm)	0.81 x 0.26 x 0.13
No. of variables in LS	277
Goodness of fit	1.146
$R_1(wR_2)$ [$F^2 > 2.0\sigma F^2$]	0.0350 (0.0988)

Table S2. Atomic Coordinates and Thermal Displacement Parameters for 3.

atom	x	y	z	U_{ani}
Ru(1)	0.244320(10)	0.174420(10)	0.721010(10)	0.01740(3)
O(1)	0.11715(6)	0.10719(7)	0.43121(9)	0.0401(3)
O(2)	0.15905(6)	-0.02471(6)	0.52849(9)	0.0331(2)
O(3)	0.44887(6)	0.17365(6)	0.95205(10)	0.0325(2)
O(4)	0.39712(6)	0.08091(7)	1.00457(8)	0.0327(2)
N(1)	0.16950(7)	0.26235(7)	0.59195(10)	0.0252(2)
N(2)	0.32381(6)	0.26656(7)	0.74709(9)	0.0246(2)
C(1)	0.24265(8)	0.10227(8)	0.59436(11)	0.0234(3)
C(2)	0.30529(8)	0.03050(9)	0.64487(12)	0.0259(3)
C(3)	0.36984(8)	0.06392(9)	0.75462(11)	0.0265(3)
C(4)	0.34192(8)	0.08072(8)	0.82037(11)	0.0230(3)
C(5)	0.16853(8)	0.06596(9)	0.50971(11)	0.0261(3)
C(6)	0.08714(9)	-0.06445(11)	0.45300(16)	0.0468(4)
C(7)	0.40105(8)	0.11709(9)	0.92794(12)	0.0253(3)
C(8)	0.44742(9)	0.11917(11)	1.10947(12)	0.0373(4)
C(9)	0.13760(7)	0.12096(9)	0.67153(11)	0.0242(3)
C(10)	0.19273(8)	0.05778(8)	0.74362(11)	0.0238(3)
C(11)	0.22119(9)	0.04796(9)	0.85888(12)	0.0290(3)
C(12)	0.24170(9)	0.14243(10)	0.91815(12)	0.0304(3)
C(13)	0.26763(8)	0.21528(9)	0.87728(11)	0.0254(3)
C(14)	0.21966(8)	0.27996(9)	0.79870(12)	0.0265(3)
C(15)	0.13753(9)	0.28278(10)	0.74442(13)	0.0334(4)
C(16)	0.09833(9)	0.18736(10)	0.69752(14)	0.0330(3)
C(17)	0.12829(8)	0.30174(9)	0.51468(13)	0.0279(3)
C(18)	0.07382(10)	0.34927(12)	0.41383(15)	0.0433(4)
C(19)	0.37095(8)	0.31573(8)	0.77283(12)	0.0255(3)
C(20)	0.43462(9)	0.37544(10)	0.81154(14)	0.0368(4)

Table S3. Anisotropic Parameters for 3.

atom	U11	U22	U33	U12	U13	U23
Ru(1)	0.01628(7)	0.01736(6)	0.01861(7)	-0.00057(3)	0.01070(5)	-0.00044(3)
O(1)	0.0345(6)	0.0478(6)	0.0250(6)	0.0077(4)	0.0115(5)	-0.0008(4)
O(2)	0.0257(5)	0.0301(5)	0.0340(6)	-0.0056(3)	0.0134(4)	-0.0089(4)
O(3)	0.0220(5)	0.0418(5)	0.0265(6)	-0.0059(3)	0.0113(5)	-0.0018(3)
O(4)	0.0276(5)	0.0422(6)	0.0196(5)	-0.0016(4)	0.0101(4)	0.0036(3)
N(1)	0.0235(5)	0.0240(4)	0.0290(6)	0.0013(4)	0.0165(5)	0.0020(4)
N(2)	0.0244(6)	0.0237(4)	0.0247(6)	-0.0005(4)	0.0146(5)	0.0014(4)
C(1)	0.0248(6)	0.0239(5)	0.0223(6)	0.0006(4)	0.0148(5)	0.0008(4)
C(2)	0.0228(6)	0.0292(6)	0.0273(7)	0.0011(5)	0.0162(5)	-0.0053(5)
C(3)	0.0193(6)	0.0312(6)	0.0273(7)	0.0018(5)	0.0134(5)	-0.0037(5)
C(4)	0.0201(6)	0.0266(6)	0.0199(6)	0.0016(4)	0.0110(5)	0.0000(4)
C(5)	0.0275(7)	0.0307(6)	0.0223(6)	0.0010(5)	0.0164(6)	-0.0030(5)
C(6)	0.0292(8)	0.0424(8)	0.0513(11)	-0.0090(6)	0.0156(8)	-0.0171(7)
C(7)	0.0216(6)	0.0280(5)	0.0245(7)	0.0035(4)	0.0131(6)	0.0028(4)
C(8)	0.0324(8)	0.0500(8)	0.0231(7)	-0.0005(6)	0.0138(7)	0.0014(6)
C(9)	0.0185(6)	0.0283(6)	0.0244(7)	-0.0039(4)	0.0124(5)	-0.0016(4)
C(10)	0.0245(6)	0.0218(5)	0.0285(7)	-0.0067(4)	0.0179(6)	-0.0009(4)
C(11)	0.0307(7)	0.0314(6)	0.0288(7)	-0.0056(5)	0.0201(6)	0.0007(5)
C(12)	0.0315(8)	0.0393(7)	0.0234(7)	-0.0034(6)	0.0182(6)	-0.0027(5)
C(13)	0.0265(7)	0.0298(6)	0.0239(7)	-0.0053(5)	0.0174(6)	-0.0070(5)
C(14)	0.0261(7)	0.0264(6)	0.0306(7)	-0.0009(5)	0.0192(6)	-0.0077(5)
C(15)	0.0304(8)	0.0365(7)	0.0379(8)	0.0033(5)	0.0233(7)	-0.0061(6)
C(16)	0.0218(7)	0.0432(7)	0.0336(8)	-0.0012(5)	0.0168(7)	-0.0048(6)
C(17)	0.0248(7)	0.0267(5)	0.0333(8)	-0.0005(5)	0.0184(6)	0.0028(5)
C(18)	0.0373(9)	0.0502(8)	0.0375(9)	0.0090(7)	0.0203(8)	0.0188(7)
C(19)	0.0240(7)	0.0257(6)	0.0256(7)	0.0010(4)	0.0146(6)	0.0046(4)
C(20)	0.0266(7)	0.0339(7)	0.0441(9)	-0.0075(5)	0.0186(7)	-0.0006(6)

Table S4. Bond Distances (Å) for 3.

atoms	Å	atoms	Å
Ru(1) – N(1)	2.0941(10)	Ru(1) – N(2)	2.0671(13)
Ru(1) – C(1)	2.2295(19)	Ru(1) – C(4)	2.2210(12)
Ru(1) – C(9)	2.1901(16)	Ru(1) – C(10)	2.1896(16)
Ru(1) – C(13)	2.2609(18)	Ru(1) – C(14)	2.2211(19)
O(1) – C(5)	1.2163(14)	O(2) – C(5)	1.3727(17)
O(2) – C(6)	1.4292(17)	O(3) – C(7)	1.2158(19)
O(4) – C(7)	1.369(2)	O(4) – C(8)	1.4263(17)
N(1) – C(17)	1.1338(17)	N(2) – C(19)	1.1310(19)
C(1) – C(2)	1.5271(19)	C(1) – C(5)	1.4665(17)
C(2) – C(3)	1.5095(16)	C(3) – C(4)	1.534(3)
C(4) – C(7)	1.4739(17)	C(9) – C(10)	1.3923(16)
C(9) – C(16)	1.523(2)	C(10) – C(11)	1.520(2)
C(11) – C(12)	1.541(2)	C(12) – C(13)	1.521(2)
C(13) – C(14)	1.3883(17)	C(14) – C(15)	1.512(2)
C(15) – C(16)	1.5456(19)	C(17) – C(18)	1.456(2)
C(19) – C(20)	1.457(2).		

Table S5. Bond Angles (deg) for 3.

atoms	deg	atoms	deg
N(1) – Ru(1) – N(2)	84.68(4)	N(1) – Ru(1) – C(1)	81.16(5)
N(1) – Ru(1) – C(4)	156.37(7)	N(1) – Ru(1) – C(9)	78.13(5)
N(1) – Ru(1) – C(10)	114.45(5)	N(1) – Ru(1) – C(13)	114.58(5)
N(1) – Ru(1) – C(14)	78.53(5)	N(2) – Ru(1) – C(1)	90.17(6)
N(2) – Ru(1) – C(4)	82.11(5)	N(2) – Ru(1) – C(9)	160.28(4)
N(2) – Ru(1) – C(10)	160.77(3)	N(2) – Ru(1) – C(13)	91.56(5)
N(2) – Ru(1) – C(14)	87.01(6)	C(1) – Ru(1) – C(4)	79.39(5)
C(1) – Ru(1) – C(9)	96.58(6)	C(1) – Ru(1) – C(10)	94.62(6)
C(1) – Ru(1) – C(13)	164.26(4)	C(1) – Ru(1) – C(14)	159.66(4)
C(4) – Ru(1) – C(9)	117.31(5)	C(4) – Ru(1) – C(10)	80.50(5)
C(4) – Ru(1) – C(13)	85.35(6)	C(4) – Ru(1) – C(14)	120.04(5)
C(9) – Ru(1) – C(10)	37.07(4)	C(9) – Ru(1) – C(13)	86.94(6)
C(9) – Ru(1) – C(14)	80.23(6)	C(10) – Ru(1) – C(13)	78.94(5)
C(10) – Ru(1) – C(14)	94.63(6)	C(13) – Ru(1) – C(14)	36.07(4)
C(5) – O(2) – C(6)	116.45(10)	C(7) – O(4) – C(8)	116.23(13)
Ru(1) – N(1) – C(17)	171.95(14)	Ru(1) – N(2) – C(19)	172.54(13)
Ru(1) – C(1) – C(2)	110.10(10)	Ru(1) – C(1) – C(5)	110.98(14)
C(2) – C(1) – C(5)	115.41(10)	C(1) – C(2) – C(3)	109.43(12)
C(2) – C(3) – C(4)	108.01(14)	Ru(1) – C(4) – C(3)	105.54(8)
Ru(1) – C(4) – C(7)	114.74(9)	C(3) – C(4) – C(7)	111.66(15)
O(1) – C(5) – O(2)	119.62(11)	O(1) – C(5) – C(1)	127.89(12)
O(2) – C(5) – C(1)	112.44(9)	O(3) – C(7) – O(4)	120.33(13)
O(3) – C(7) – C(4)	127.44(19)	O(4) – C(7) – C(4)	112.22(14)
Ru(1) – C(9) – C(10)	71.45(9)	Ru(1) – C(9) – C(16)	113.40(8)
C(10) – C(9) – C(16)	124.62(16)	Ru(1) – C(10) – C(9)	71.48(9)
Ru(1) – C(10) – C(11)	112.78(8)	C(9) – C(10) – C(11)	123.34(17)
C(10) – C(11) – C(12)	113.32(12)	C(11) – C(12) – C(13)	113.03(17)
Ru(1) – C(13) – C(12)	113.27(9)	Ru(1) – C(13) – C(14)	70.40(10)

Table S5. continued.

atoms	deg	atoms	deg
C(12) – C(13) – C(14)	122.30(15)	Ru(1) – C(14) – C(13)	73.52(10)
Ru(1) – C(14) – C(15)	110.50(9)	C(13) – C(14) – C(15)	123.43(17)
C(14) – C(15) – C(16)	113.70(14)	C(9) – C(16) – C(15)	114.38(17)
N(1) – C(17) – C(18)	177.96(14)	N(2) – C(19) – C(20)	176.55(13)

Table S6. Torsion Angles (deg) for 3.

atoms	deg
N(1) – Ru(1) – N(2) – C(19)	141.3(10)
N(2) – Ru(1) – N(1) – C(17)	106.9(12)
N(1) – Ru(1) – C(1) – C(2)	168.07(11)
N(1) – Ru(1) – C(1) – C(5)	62.90(9)
C(1) – Ru(1) – N(1) – C(17)	15.9(12)
N(1) – Ru(1) – C(4) – C(3)	-8.18(14)
N(1) – Ru(1) – C(4) – C(7)	115.18(16)
C(4) – Ru(1) – N(1) – C(17)	50.8(12)
N(1) – Ru(1) – C(9) – C(10)	168.45(11)
N(1) – Ru(1) – C(9) – C(16)	-71.04(11)
C(9) – Ru(1) – N(1) – C(17)	-82.8(12)
N(1) – Ru(1) – C(10) – C(9)	-12.43(12)
N(1) – Ru(1) – C(10) – C(11)	-131.64(11)
C(10) – Ru(1) – N(1) – C(17)	-75.2(12)
N(1) – Ru(1) – C(13) – C(12)	115.56(10)
N(1) – Ru(1) – C(13) – C(14)	-2.10(11)
C(13) – Ru(1) – N(1) – C(17)	-163.8(11)
N(1) – Ru(1) – C(14) – C(13)	178.05(10)
N(1) – Ru(1) – C(14) – C(15)	57.86(11)
C(14) – Ru(1) – N(1) – C(17)	-165.1(12)
N(2) – Ru(1) – C(1) – C(2)	83.49(11)
N(2) – Ru(1) – C(1) – C(5)	-147.48(9)
C(1) – Ru(1) – N(2) – C(19)	-137.6(9)
N(2) – Ru(1) – C(4) – C(3)	-64.77(8)
N(2) – Ru(1) – C(4) – C(7)	58.59(14)
C(4) – Ru(1) – N(2) – C(19)	-58.3(9)
N(2) – Ru(1) – C(9) – C(10)	-161.73(16)
N(2) – Ru(1) – C(9) – C(16)	-41.2(2)

Table S6. continued.

atoms	deg
C(9) – Ru(1) – N(2) – C(19)	112.1(9)
N(2) – Ru(1) – C(10) – C(9)	161.26(17)
N(2) – Ru(1) – C(10) – C(11)	42.1(2)
C(10) – Ru(1) – N(2) – C(19)	-32.9(10)
N(2) – Ru(1) – C(13) – C(12)	-159.58(10)
N(2) – Ru(1) – C(13) – C(14)	82.76(10)
C(13) – Ru(1) – N(2) – C(19)	26.8(9)
N(2) – Ru(1) – C(14) – C(13)	-96.78(9)
N(2) – Ru(1) – C(14) – C(15)	143.03(11)
C(14) – Ru(1) – N(2) – C(19)	62.6(9)
C(1) – Ru(1) – C(4) – C(3)	26.89(8)
C(1) – Ru(1) – C(4) – C(7)	150.25(15)
C(4) – Ru(1) – C(1) – C(2)	1.55(11)
C(4) – Ru(1) – C(1) – C(5)	130.58(10)
C(1) – Ru(1) – C(9) – C(10)	88.96(10)
C(1) – Ru(1) – C(9) – C(16)	-150.53(10)
C(9) – Ru(1) – C(1) – C(2)	-115.08(11)
C(9) – Ru(1) – C(1) – C(5)	13.95(9)
C(1) – Ru(1) – C(10) – C(9)	-94.81(10)
C(1) – Ru(1) – C(10) – C(11)	145.98(11)
C(10) – Ru(1) – C(1) – C(2)	-77.87(11)
C(10) – Ru(1) – C(1) – C(5)	51.16(9)
C(1) – Ru(1) – C(13) – C(12)	-63.4(2)
C(1) – Ru(1) – C(13) – C(14)	178.9(2)
C(13) – Ru(1) – C(1) – C(2)	-12.9(2)
C(13) – Ru(1) – C(1) – C(5)	116.2(2)
C(1) – Ru(1) – C(14) – C(13)	-179.16(15)
C(1) – Ru(1) – C(14) – C(15)	60.7(2)

Table S6. continued.

atoms	deg
C(14) – Ru(1) – C(1) – C(2)	165.30(15)
C(14) – Ru(1) – C(1) – C(5)	-65.7(2)
C(4) – Ru(1) – C(9) – C(10)	7.53(12)
C(4) – Ru(1) – C(9) – C(16)	128.04(11)
C(9) – Ru(1) – C(4) – C(3)	118.87(9)
C(9) – Ru(1) – C(4) – C(7)	-117.77(14)
C(4) – Ru(1) – C(10) – C(9)	-173.22(11)
C(4) – Ru(1) – C(10) – C(11)	67.57(12)
C(10) – Ru(1) – C(4) – C(3)	123.46(8)
C(10) – Ru(1) – C(4) – C(7)	-113.18(15)
C(4) – Ru(1) – C(13) – C(12)	-77.63(10)
C(4) – Ru(1) – C(13) – C(14)	164.70(10)
C(13) – Ru(1) – C(4) – C(3)	-157.00(8)
C(13) – Ru(1) – C(4) – C(7)	-33.64(15)
C(4) – Ru(1) – C(14) – C(13)	-17.68(12)
C(4) – Ru(1) – C(14) – C(15)	-137.87(11)
C(14) – Ru(1) – C(4) – C(3)	-146.66(8)
C(14) – Ru(1) – C(4) – C(7)	-23.30(17)
C(9) – Ru(1) – C(10) – C(11)	-119.21(17)
C(10) – Ru(1) – C(9) – C(16)	120.51(16)
C(9) – Ru(1) – C(13) – C(12)	40.09(10)
C(9) – Ru(1) – C(13) – C(14)	-77.57(10)
C(13) – Ru(1) – C(9) – C(10)	-75.64(10)
C(13) – Ru(1) – C(9) – C(16)	44.87(11)
C(9) – Ru(1) – C(14) – C(13)	98.30(10)
C(9) – Ru(1) – C(14) – C(15)	-21.88(11)
C(14) – Ru(1) – C(9) – C(10)	-111.34(10)
C(14) – Ru(1) – C(9) – C(16)	9.17(11)

Table S6. continued.

atoms	deg
C(10) – Ru(1) – C(13) – C(12)	3.58(10)
C(10) – Ru(1) – C(13) – C(14)	-114.08(10)
C(13) – Ru(1) – C(10) – C(9)	99.70(10)
C(13) – Ru(1) – C(10) – C(11)	-19.51(11)
C(10) – Ru(1) – C(14) – C(13)	64.02(10)
C(10) – Ru(1) – C(14) – C(15)	-56.17(11)
C(14) – Ru(1) – C(10) – C(9)	67.06(10)
C(14) – Ru(1) – C(10) – C(11)	-52.14(11)
C(13) – Ru(1) – C(14) – C(15)	-120.19(17)
C(14) – Ru(1) – C(13) – C(12)	117.66(15)
C(6) – O(2) – C(5) – O(1)	-0.9(3)
C(6) – O(2) – C(5) – C(1)	176.83(19)
C(8) – O(4) – C(7) – O(3)	5.1(2)
C(8) – O(4) – C(7) – C(4)	-173.84(13)
Ru(1) – N(1) – C(17) – C(18)	44(8)
Ru(1) – N(2) – C(19) – C(20)	35(4)
Ru(1) – C(1) – C(2) – C(3)	-30.93(18)
Ru(1) – C(1) – C(5) – O(1)	86.0(2)
Ru(1) – C(1) – C(5) – O(2)	-91.47(15)
C(2) – C(1) – C(5) – O(1)	-147.9(2)
C(2) – C(1) – C(5) – O(2)	34.7(2)
C(5) – C(1) – C(2) – C(3)	-157.51(17)
C(1) – C(2) – C(3) – C(4)	56.29(17)
C(2) – C(3) – C(4) – Ru(1)	-52.55(10)
C(2) – C(3) – C(4) – C(7)	-177.85(10)
Ru(1) – C(4) – C(7) – O(3)	-81.1(2)
Ru(1) – C(4) – C(7) – O(4)	97.75(12)
C(3) – C(4) – C(7) – O(3)	38.9(2)

Table S6. continued.

atoms	deg
C(3) – C(4) – C(7) – O(4)	-142.22(12)
Ru(1) – C(9) – C(10) – C(11)	105.57(13)
Ru(1) – C(9) – C(16) – C(15)	5.07(17)
C(10) – C(9) – C(16) – C(15)	88.0(2)
C(16) – C(9) – C(10) – Ru(1)	-106.11(13)
C(16) – C(9) – C(10) – C(11)	-0.5(2)
Ru(1) – C(10) – C(11) – C(12)	32.79(19)
C(9) – C(10) – C(11) – C(12)	-49.4(2)
C(10) – C(11) – C(12) – C(13)	-29.7(2)
C(11) – C(12) – C(13) – Ru(1)	12.74(15)
C(11) – C(12) – C(13) – C(14)	93.53(19)
Ru(1) – C(13) – C(14) – C(15)	104.03(15)
C(12) – C(13) – C(14) – Ru(1)	-105.73(14)
C(12) – C(13) – C(14) – C(15)	-1.7(2)
Ru(1) – C(14) – C(15) – C(16)	31.2(2)
C(13) – C(14) – C(15) – C(16)	-52.2(2)
C(14) – C(15) – C(16) – C(9)	-24.3(2)

Table S7. Physical and Crystallographic Parameters for 2·0.5THF.

	2·0.5THF
Formula	$C_{18}H_{28}O_{4.5}Ru$
Formula weight	417.49
Crystal system	*triclinic*
Space group	*P*-1 (*No.*2)
Unit cell dimensions	
a (Å)	8.825(6)
b (Å)	10.789(7)
c (Å)	14.936(10)
α (deg)	69.75(3)
β (deg)	73.68(3)
γ (deg)	72.17(3)
V (Å^3)	1245.5(14)
Z	2
D_{calcd} (g cm^{-1})	1.113
Temp (K)	200.0
F(000)	432.00
μ (mm^{-1})	0.644
Reflns number total	6472
No. of observed eflections [$F^2>2\sigma(F^2)$]	5698
Crystal size (mm)	0.34 x 0.18 x 0.13
No. of variables in LS	212
Goodness of fit	1.416
$R_1(wR_2)$ [$F^2 > 2.0\sigma F^2$]	0.0972 (0.3203)

Table S8. Atomic Coordinates and Thermal Displacement Parameters for 2·0.5THF.

atom	x	y	z	$U_{ani(or\ iso)}$
Ru(1)	0.88169(4)	0.11685(3)	0.62991(2)	0.0357(2)
O(1)	1.1757(4)	0.0353(3)	0.4171(2)	0.0409(7)
O(2)	0.8856(6)	-0.0460(4)	0.7768(3)	0.0485(9)
O(3)	1.2769(4)	0.1623(4)	0.4640(3)	0.0477(8)
O(4)	0.9615(7)	-0.0019(6)	0.8919(3)	0.0698(14)
O(5)	0.355(2)	0.670(2)	-0.0312(17)	0.137(6)
C(1)	1.1388(6)	0.0079(6)	0.5886(4)	0.0428(10)
C(2)	1.2392(6)	0.0073(7)	0.6580(4)	0.0496(13)
C(3)	1.1687(7)	0.1329(7)	0.6956(4)	0.0517(13)
C(4)	0.9862(6)	0.1516(6)	0.7272(4)	0.0459(11)
C(5)	1.1967(5)	0.0644(5)	0.4851(4)	0.0387(9)
C(6)	0.9425(7)	0.0273(6)	0.8015(4)	0.0484(11)
C(7)	1.3287(7)	0.2289(6)	0.3649(4)	0.0527(13)
C(8)	0.9130(15)	-0.1278(10)	0.9624(5)	0.093(3)
C(9)	0.6646(6)	0.2441(5)	0.7027(4)	0.0440(10)
C(10)	0.6125(6)	0.1747(5)	0.6550(4)	0.0440(10)
C(11)	0.5608(6)	0.2374(6)	0.5598(5)	0.0500(13)
C(12)	0.6766(6)	0.3198(6)	0.4796(4)	0.0467(11)
C(13)	0.8528(6)	0.2656(5)	0.4950(4)	0.0372(9)
C(14)	0.9193(6)	0.3146(4)	0.5482(4)	0.0414(10)
C(15)	0.8216(7)	0.4268(5)	0.5973(4)	0.0498(12)
C(16)	0.6616(7)	0.3940(6)	0.6633(5)	0.0539(13)
C(17)	0.368(3)	0.710(3)	0.044(2)	0.120(8)
C(18)	0.475(3)	0.838(3)	-0.004(2)	0.124(8)
C(19)	0.491(3)	0.856(3)	-0.112(2)	0.118(8)
C(20)	0.470(3)	0.717(3)	-0.109(2)	0.116(7)

Table S9. Anisotropic Parameters for 2·0.5 THF.

atom	U11	U22	U33	U12	U13	U23
Ru(1)	0.0295(2)	0.0365(3)	0.0469(3)	-0.01134(19)	-0.0086(2)	-0.0148(2)
O(1)	0.0333(15)	0.0422(18)	0.0552(19)	-0.0144(13)	-0.0113(14)	-0.0167(15)
O(2)	0.066(2)	0.042(2)	0.0464(19)	-0.0200(19)	-0.0174(18)	-0.0125(15)
O(3)	0.0378(17)	0.054(2)	0.063(2)	-0.0205(16)	-0.0057(16)	-0.0251(18)
O(4)	0.092(3)	0.088(3)	0.046(2)	-0.041(3)	-0.024(2)	-0.013(2)
C(1)	0.032(2)	0.043(2)	0.061(2)	-0.0054(19)	-0.016(2)	-0.021(2)
C(2)	0.029(2)	0.061(3)	0.065(3)	-0.011(2)	-0.017(2)	-0.018(2)
C(3)	0.051(2)	0.068(3)	0.055(2)	-0.029(2)	-0.021(2)	-0.017(2)
C(4)	0.045(2)	0.051(2)	0.054(2)	-0.015(2)	-0.015(2)	-0.022(2)
C(5)	0.0230(17)	0.036(2)	0.062(2)	-0.0039(15)	-0.0115(18)	-0.0212(19)
C(6)	0.044(2)	0.057(3)	0.053(2)	-0.010(2)	-0.016(2)	-0.022(2)
C(7)	0.042(2)	0.054(3)	0.069(3)	-0.024(2)	-0.005(2)	-0.019(2)
C(8)	0.145(9)	0.095(6)	0.053(3)	-0.058(6)	-0.034(4)	-0.001(3)
C(9)	0.035(2)	0.040(2)	0.058(2)	-0.0055(19)	-0.002(2)	-0.024(2)
C(10)	0.029(2)	0.040(2)	0.061(2)	-0.0103(18)	-0.0040(19)	-0.014(2)
C(11)	0.028(2)	0.049(3)	0.078(3)	-0.009(2)	-0.015(2)	-0.021(2)
C(12)	0.037(2)	0.044(2)	0.055(2)	-0.0014(19)	-0.013(2)	-0.013(2)
C(13)	0.033(2)	0.033(2)	0.048(2)	-0.0110(17)	-0.0091(18)	-0.0094(17)
C(14)	0.033(2)	0.030(2)	0.061(2)	-0.0098(16)	-0.005(2)	-0.0147(18)
C(15)	0.046(2)	0.036(2)	0.070(3)	-0.010(2)	-0.004(2)	-0.024(2)
C(16)	0.042(2)	0.046(3)	0.079(3)	-0.009(2)	-0.006(2)	-0.029(2)

Table S10. Bond Distances (Å) for 2·0.5 THF.

atoms	Å	atoms	Å
Ru(1) – O(1)	2.225(5)	Ru(1) – O(2)	2.289(3)
Ru(1) – C(1)	2.235(4)	Ru(1) – C(4)	2.109(7)
Ru(1) – C(9)	2.233(5)	Ru(1) – C(10)	2.220(4)
Ru(1) – C(13)	2.122(5)	Ru(1) – C(14)	2.134(4)
O(1) – C(5)	1.235(8)	O(2) – C(6)	1.250(10)
O(3) – C(5)	1.348(7)	O(3) – C(7)	1.415(7)
O(4) – C(6)	1.324(8)	O(4) – C(8)	1.500(11)
O(5) – C(17)	1.38(5)	O(5) – C(20)	1.38(3)
C(1) – C(2)	1.538(10)	C(1) – C(5)	1.455(7)
C(2) – C(3)	1.533(11)	C(3) – C(4)	1.516(8)
C(4) – C(6)	1.492(8)	C(9) – C(10)	1.483(9)
C(9) – C(16)	1.512(8)	C(10) – C(11)	1.428(11)
C(11) – C(12)	1.549(8)	C(12) – C(13)	1.537(8)
C(13) – C(14)	1.413(10)	C(14) – C(15)	1.538(8)
C(15) – C(16)	1.541(8)	C(17) – C(18)	1.74(5)
C(18) – C(19)	1.52(4)	C(19) – C(20)	1.55(5)

Table S11. Bond Angles (deg) for 2·0.5 THF.

atoms	deg	atoms	deg
O(1) – Ru(1) – O(2)	84.99(17)	O(1) – Ru(1) – C(1)	83.9(2)
O(1) – Ru(1) – C(4)	146.91(18)	O(1) – Ru(1) – C(9)	114.0(2)
O(1) – Ru(1) – C(10)	77.6(2)	O(1) – Ru(1) – C(13)	91.5(2)
O(1) – Ru(1) – C(14)	129.6(2)	O(2) – Ru(1) – C(1)	85.14(17)
O(2) – Ru(1) – C(4)	64.8(2)	O(2) – Ru(1) – C(9)	88.19(17)
O(2) – Ru(1) – C(10)	93.23(19)	O(2) – Ru(1) – C(13)	173.9(2)
O(2) – Ru(1) – C(14)	145.3(2)	C(1) – Ru(1) – C(4)	80.5(2)
C(1) – Ru(1) – C(9)	160.3(2)	C(1) – Ru(1) – C(10)	161.4(2)
C(1) – Ru(1) – C(13)	99.46(19)	C(1) – Ru(1) – C(14)	95.23(19)
C(4) – Ru(1) – C(9)	79.9(2)	C(4) – Ru(1) – C(10)	115.5(2)
C(4) – Ru(1) – C(13)	119.7(2)	C(4) – Ru(1) – C(14)	81.0(2)
C(9) – Ru(1) – C(10)	37.4(2)	C(9) – Ru(1) – C(13)	88.72(19)
C(9) – Ru(1) – C(14)	79.91(19)	C(10) – Ru(1) – C(13)	81.1(2)
C(10) – Ru(1) – C(14)	96.53(19)	C(13) – Ru(1) – C(14)	38.8(2)
Ru(1) – O(1) – C(5)	146.7(3)	Ru(1) – O(2) – C(6)	87.3(3)
C(5) – O(3) – C(7)	118.1(5)	C(6) – O(4) – C(8)	116.5(7)
C(17) – O(5) – C(20)	105(3)	Ru(1) – C(1) – C(2)	109.4(4)
Ru(1) – C(1) – C(5)	109.0(3)	C(2) – C(1) – C(5)	116.7(5)
C(1) – C(2) – C(3)	110.7(4)	C(2) – C(3) – C(4)	109.1(6)
Ru(1) – C(4) – C(3)	112.4(4)	Ru(1) – C(4) – C(6)	88.7(4)
C(3) – C(4) – C(6)	111.2(4)	O(1) – C(5) – O(3)	118.4(4)
O(1) – C(5) – C(1)	127.3(5)	O(3) – C(5) – C(1)	114.2(5)
O(2) – C(6) – O(4)	121.5(5)	O(2) – C(6) – C(4)	118.8(5)
O(4) – C(6) – C(4)	119.7(7)	Ru(1) – C(9) – C(10)	70.8(3)
Ru(1) – C(9) – C(16)	112.8(3)	C(10) – C(9) – C(16)	122.7(5)
Ru(1) – C(10) – C(9)	71.8(3)	Ru(1) – C(10) – C(11)	109.1(3)
C(9) – C(10) – C(11)	124.6(5)	C(10) – C(11) – C(12)	114.5(5)

Table S11. continued

atoms	deg	atoms	deg
C(11) – C(12) – C(13)	111.9(4)	Ru(1) – C(13) – C(12)	114.4(3)
Ru(1) – C(13) – C(14)	71.1(3)	C(12) – C(13) – C(14)	123.5(5)
Ru(1) – C(14) – C(13)	70.1(3)	Ru(1) – C(14) – C(15)	114.4(3)
C(13) – C(14) – C(15)	123.2(4)	C(14) – C(15) – C(16)	111.7(5)
C(9) – C(16) – C(15)	114.3(4)	O(5) – C(17) – C(18)	109(2)
C(17) – C(18) – C(19)	99(2)	C(18) – C(19) – C(20)	101(2)
O(5) – C(20) – C(19)	112(2)		

Table S12. Torsion Angles (deg) for 2·0.5 THF.

atoms	deg
O(1) – Ru(1) – O(2) C(6)	170.3(3)
O(2) – Ru(1) – O(1) – C(5)	-174.0(5)
O(1) – Ru(1) – C(1) – C(2)	-145.4(3)
O(1) – Ru(1) – C(1) – C(5)	86.0(4)
C(1) – Ru(1) – O(1) – C(5)	-88.4(5)
O(1) – Ru(1) – C(4) – C(3)	82.7(4)
O(1) – Ru(1) – C(4) – C(6)	-29.8(4)
C(4) – Ru(1) – O(1) – C(5)	-150.4(5)
O(1) – Ru(1) – C(9) – C(10)	-14.0(3)
O(1) – Ru(1) – C(9) – C(16)	-132.3(5)
C(9) – Ru(1) – O(1) – C(5)	100.2(5)
O(1) – Ru(1) – C(10) – C(9)	166.9(3)
O(1) – Ru(1) – C(10) – C(11)	-71.9(4)
C(10) – Ru(1) – O(1) – C(5)	91.6(5)
O(1) – Ru(1) – C(13) – C(12)	70.4(4)
O(1) – Ru(1) – C(13) – C(14)	-170.6(2)
C(13) – Ru(1) – O(1) – C(5)	11.0(5)
O(1) – Ru(1) – C(14) – C(13)	12.2(3)
O(1) – Ru(1) – C(14) – C(15)	130.6(4)
C(14) – Ru(1) – O(1) – C(5)	3.3(6)
O(2) – Ru(1) – C(1) – C(2)	-59.9(4)
O(2) – Ru(1) – C(1) – C(5)	171.5(5)
C(1) – Ru(1) – O(2) – C(6)	86.0(3)
O(2) – Ru(1) – C(4) – C(3)	108.8(4)
O(2) – Ru(1) – C(4) – C(6)	-3.6(2)
C(4) – Ru(1) – O(2) – C(6)	4.3(3)
O(2) – Ru(1) – C(9) – C(10)	-97.7(3)
O(2) – Ru(1) – C(9) – C(16)	144.0(5)
C(9) – Ru(1) – O(2) – C(6)	-75.4(3)

Table S12. continued.

atoms	deg
O(2) – Ru(1) – C(10) – C(9)	82.8(3)
O(2) – Ru(1) – C(10) – C(11)	-156.0(4)
C(10) – Ru(1) – O(2) – C(6)	-112.5(3)
O(2) – Ru(1) – C(13) – C(12)	16(2)
O(2) – Ru(1) – C(13) – C(14)	135.1(19)
C(13) – Ru(1) – O(2) – C(6)	-135.1(19)
O(2) – Ru(1) – C(14) – C(13)	-172.4(3)
O(2) – Ru(1) – C(14) – C(15)	-54.0(5)
C(14) – Ru(1) – O(2) – C(6)	-6.1(5)
C(1) – Ru(1) – C(4) – C(3)	19.8(4)
C(1) – Ru(1) – C(4) – C(6)	-92.7(3)
C(4) – Ru(1) – C(1) – C(2)	5.4(3)
C(4) – Ru(1) – C(1) – C(5)	-123.3(5)
C(1) – Ru(1) – C(9) – C(10)	-167.9(5)
C(1) – Ru(1) – C(9) – C(16)	73.9(7)
C(9) – Ru(1) – C(1) – C(2)	10.7(8)
C(9) – Ru(1) – C(1) – C(5)	-117.9(6)
C(1) – Ru(1) – C(10) – C(9)	167.1(5)
C(1) – Ru(1) – C(10) – C(11)	-71.7(7)
C(10) – Ru(1) – C(1) – C(2)	-145.6(6)
C(10) – Ru(1) – C(1) – C(5)	85.8(7)
C(1) – Ru(1) – C(13) – C(12)	154.4(4)
C(1) – Ru(1) – C(13) – C(14)	-86.6(3)
C(13) – Ru(1) – C(1) – C(2)	124.2(4)
C(13) – Ru(1) – C(1) – C(5)	-4.5(5)
C(1) – Ru(1) – C(14) – C(13)	98.6(3)
C(1) – Ru(1) – C(14) – C(15)	-143.0(4)
C(14) – Ru(1) – C(1) – C(2)	85.3(4)
C(14) – Ru(1) – C(1) – C(5)	-43.4(5)

Table S12. continued.

atoms	deg
C(4) – Ru(1) – C(9) – C(10)	-162.5(3)
C(4) – Ru(1) – C(9) – C(16)	79.3(5)
C(9) – Ru(1) – C(4) – C(3)	-158.4(4)
C(9) – Ru(1) – C(4) – C(6)	89.2(3)
C(4) – Ru(1) – C(10) – C(9)	19.2(3)
C(4) – Ru(1) – C(10) – C(11)	140.4(4)
C(10) – Ru(1) – C(4) – C(3)	-170.1(3)
C(10) – Ru(1) – C(4) – C(6)	77.5(3)
C(4) – Ru(1) – C(13) – C(12)	-121.2(4)
C(4) – Ru(1) – C(13) – C(14)	-2.2(3)
C(13) – Ru(1) – C(4) – C(3)	-75.7(4)
C(13) – Ru(1) – C(4) – C(6)	171.8(2)
C(4) – Ru(1) – C(14) – C(13)	178.1(3)
C(4) – Ru(1) – C(14) – C(15)	-63.5(4)
C(14) – Ru(1) – C(4) – C(3)	-77.1(4)
C(14) – Ru(1) – C(4) – C(6)	170.4(3)
C(9) – Ru(1) – C(10) – C(11)	121.2(5)
C(10) – Ru(1) – C(9) – C(16)	-118.3(6)
C(9) – Ru(1) – C(13) – C(12)	-43.6(5)
C(9) – Ru(1) – C(13) – C(14)	75.4(3)
C(13) – Ru(1) – C(9) – C(10)	77.0(3)
C(13) – Ru(1) – C(9) – C(16)	-41.3(5)
C(9) – Ru(1) – C(14) – C(13)	-100.7(3)
C(9) – Ru(1) – C(14) – C(15)	17.7(4)
C(14) – Ru(1) – C(9) – C(10)	115.0(3)
C(14) – Ru(1) – C(9) – C(16)	-3.3(5)
C(10) – Ru(1) – C(13) – C(12)	-6.8(4)
C(10) – Ru(1) – C(13) – C(14)	112.2(3)
C(13) – Ru(1) – C(10) – C(9)	-99.6(3)

Table S12. continued.

atoms	deg
C(13) – Ru(1) – C(10) – C(11)	21.6(4)
C(10) – Ru(1) – C(14) – C(13)	-67.0(3)
C(10) – Ru(1) – C(14) – C(15)	51.4(5)
C(14) – Ru(1) – C(10) – C(9)	-63.9(3)
C(14) – Ru(1) – C(10) – C(11)	57.3(5)
C(13) – Ru(1) – C(14) – C(15)	118.4(5)
C(14) – Ru(1) – C(13) – C(12)	-119.0(5)
Ru(1) – O(1) – C(5) – O(3)	161.1(3)
Ru(1) – O(1) – C(5) – C(1)	-21.4(8)
Ru(1) – O(2) – C(6) – O(4)	172.4(5)
Ru(1) – O(2) – C(6) – C(4)	-6.3(4)
C(7) – O(3) – C(5) – O(1)	1.7(6)
C(7) – O(3) – C(5) – C(1)	-176.1(4)
C(8) – O(4) – C(6) – O(2)	0.6(9)
C(8) – O(4) – C(6) – C(4)	179.3(6)
C(17) – O(5) – C(20) – C(19)	-35(3)
C(20) – O(5) – C(17) – C(18)	17(2)
Ru(1) – C(1) – C(2) – C(3)	-29.2(5)
Ru(1) – C(1) – C(5) – O(1)	-82.9(5)
Ru(1) – C(1) – C(5) – O(3)	94.7(4)
C(2) – C(1) – C(5) – O(1)	152.6(5)
C(2) – C(1) – C(5) – O(3)	-29.7(6)
C(5) – C(1) – C(2) – C(3)	95.1(5)
C(1) – C(2) – C(3) – C(4)	46.1(5)
C(2) – C(3) – C(4) – Ru(1)	-41.7(5)
C(2) – C(3) – C(4) – C(6)	56.0(7)
Ru(1) – C(4) – C(6) – O(2)	6.8(5)
Ru(1) – C(4) – C(6) – O(4)	-171.9(4)
C(3) – C(4) – C(6) – O(2)	-106.8(6)

Table S12. continued.

atoms	deg
C(3) – C(4) – C(6) – O(4)	74.5(7)
Ru(1) – C(9) – C(10) – C(11)	-101.0(4)
Ru(1) – C(9) – C(16) – C(15)	-11.7(8)
C(10) – C(9) – C(16) – C(15)	-92.8(7)
C(16) – C(9) – C(10) – Ru(1)	105.3(4)
C(16) – C(9) – C(10) – C(11)	4.3(7)
Ru(1) – C(10) – C(11) – C(12)	-33.2(6)
C(9) – C(10) – C(11) – C(12)	47.5(7)
C(10) – C(11) – C(12) – C(13)	28.5(8)
C(11) – C(12) – C(13) – Ru(1)	-8.8(7)
C(11) – C(12) – C(13) – C(14)	-91.6(7)
Ru(1) – C(13) – C(14) – C(15)	-106.8(4)
C(12) – C(13) – C(14) – Ru(1)	107.3(4)
C(12) – C(13) – C(14) – C(15)	0.6(7)
Ru(1) – C(14) – C(15) – C(16)	-29.0(6)
C(13) – C(14) – C(15) – C(16)	52.4(7)
C(14) – C(15) – C(16) – C(9)	26.0(8)
O(5) – C(17) – C(18) – C(19)	5(2)
C(17) – C(18) – C(19) – C(20)	-22(2)
C(18) – C(19) – C(20) – O(5)	38(3)

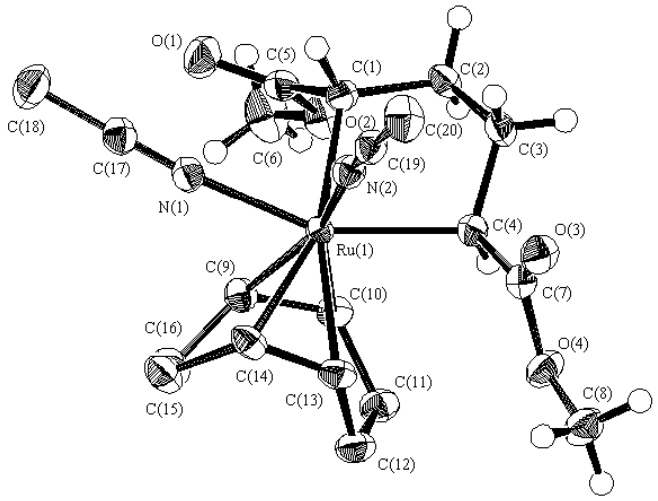

Figure S1. Molecular structure of 3 with numbering schemes. All hydrogen atoms except the ruthenacyclopentane fragment are omitted for clarity. Thermal ellipsoids represent 50% probability.

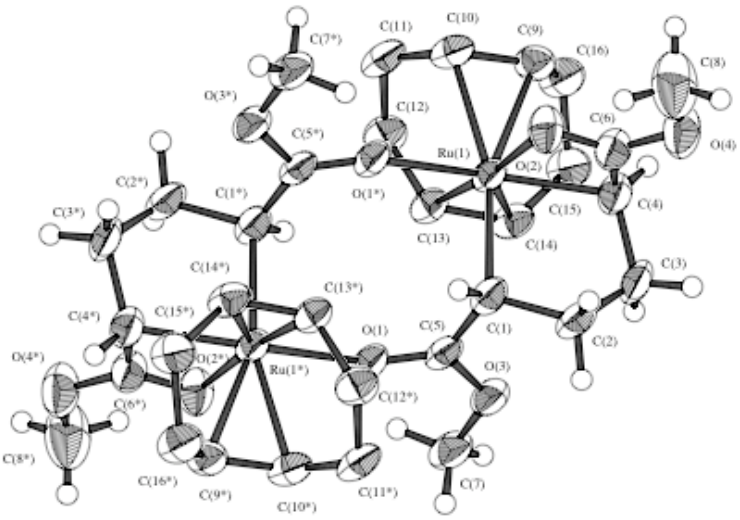

Figure S2. Molecular Structure of 2 with numbering schemes. Atoms with a number having asterisk are placed by symmetrical operation on the basis of the space group. All hydrogen atoms except the ruthenacyclopentane fragment and incorporated THF molecule are omitted for clarity. Thermal ellipsoids represent 50% probability.

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