Supporting Information for the Communication:

Synthesis and Characterization of Triruthenium Complexes Containing a Perpendicularly Coordinated Alkyne Ligand

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General Procedures. All experiments were carried out under an argon atmosphere. All compounds were treated with Schlenk techniques. Dehydrated toluene, tetrahydrofuran, and pentane used in this study were purchased from Kanto Chemicals and stored under an argon atmosphere. Benzene-d_6, THF-d_8, and toluene-d_8 were dried over sodium-benzophenone ketyl and stored under an argon atmosphere. Complex **1** was prepared according to a recently published method in the reference 6 (Suzuki, H.; Kakigano, K.; Tada, K.; Igarashi, M.; Matsubara, K.; Inagaki, A.; Ohshima, M.; Takao, T. *Bull. Chem. Soc., Jpn.* in press). IR spectra were recorded on a Nicolet AVATAR 360 E.S.P. spectrophotometer and a Jasco FT/IR-5000 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer and a JEOL GSX-500 spectrometer with tetramethylsilane as an internal standard. Elemental analyses of **2a**, **2b**, and **2c** were performed by the Analytical Facility at the Research Laboratory of Resources Utilization, Tokyo Institute of Technology. Product analysis was carried out on a HITACHI G-3000 gas chromatograph equipped with a GL Science capillary column TC-WAX (30m × 0.25mm), and recorded on a HITACHI D-2500 Chromato-Integrator.

X-ray Structure Determination. X-ray-quality crystal of **2a** was obtained directly from the preparations described below and mounted on glass fibers. Diffraction experiments were performed on a Rigaku RAXIS-RAPID imaging plate at -120 ºC with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). The structure of **2a** was solved by a direct method and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculation on F^2 using SHELX-97 program package. The positions of hydrogen atoms bonded to the ruthenium atoms of **2a** were located by sequential difference Fourier synthesis and were refined isotropically. Neutral atom scattering factors were obtained from the standard sources.[1] Crystal data and results of the analyses are listed in Table S-1.

Table S-1. Crystallographic Data for 2a

(a) Crystal Data		(b) Intensity Measurements	
Empirical Formula	C38 H54 Ru3	Diffractometer	Rigaku RAXIS-RAPID
Formula Weight	814.02	Radiation	Mo Kα (λ = 0.71069 Å)
Crystal Description	block	Monochrometer	Graphite
Crystal Color	Dark-green	2θmax	60.1°
Crystal Size	0.40×0.40×0.30 mm	Reflections Collected	20349
Crystallizing Solution	THF/pentane (- 30°C)	Independent reflections	5204 (R_{int} = 5.8571)
Crystal System	Monoclinic	Reflections Observed (> 2σ)	4191
Space Group	C_2/m (#12)	Abs. Correction type	Empirical
Lattice Parameters	a = 17.083(6) Å	Abs. Transmission	0.5456 (min.), 1.0000 (max.)
	b = 18.356(6) Å		
	c = 11.473(4) Å	(c) Refinement (Shelxl-97)	
		R_1 (I > 2σ(I))	0.0468
	β = 105.732(15)°	wR_2 (I > 2σ(I))	0.1166
		R_1 (all data)	0.0607
volume	3463(2) Å^3	wR_2 (all data)	0.1252
Z value	4	Data / Restraints / Parameters	5186 / 0 / 206
D_{calc}	1.561 g/cm^3	GOF	1.028
Measurement Temp	153(2) K	Largest diff. Prak and hole	1.439 and -1.367 e.Å^{-3}
μ(Mo Kα)	1.316 mm $^{-1}$		

(1) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U. K., 1975; Vol. 4.

Experimental Section

Preparation of {Cp*Ru(μ-H)}$_3$(μ_3-η^2:η^2(⊥)-PhCCH) (2a). A 50-mL flask was charged with THF (20 mL) and a triruthenium pentahydrido complex {Cp*Ru(μ-H)}$_3$(μ-H)$_2$ (**1**; 140 mg, 0.196 mmol). Phenylacetylene (26 μL, 0.237 mmol) was added with vigorous stirring. The solution was allowed to react for 1h at 25°C, and the color of the solution turned from dark-purple to dark-green. The solvent and remaining phenylacetylene were then removed under reduced pressure, and 160 mg of **2a** was obtained as a dark-green solid (99% yield). A single-crystal used for the diffraction studies was prepared from the THF/pentane solution stored at -30°C. ^{1}H NMR (400 MHz, THF-d_8, -20ºC, TMS): δ 9.88 (s, 1H, C*H*), 6.72 (t, J_{H-H} = 7.6 Hz, 2H, Ph-*meta*), 6.48 (t, J_{H-H} = 7.6 Hz, 1H, Ph-*para*), 5.60 (d, J_{H-H} = 7.6 Hz, 2H, Ph-*ortho*), 1.95 (s,

30H, C_5Me_5), 1.55 (s, 15H, C_5Me_5), -6.78 (d, J_{H-H} = 3.2 Hz, 2H, Ru*H*), -24.40 (t, J_{H-H} = 3.2 Hz, 1H, Ru*H*). ^{13}C NMR (100 MHz, toluene-d_8, -40ºC, TMS): δ 178.7 (d, J_{C-H} = 183.4 Hz, -*C*H), 148.1 (s, *Ph-ipso*), 126.4 (d, J_{C-H} = 159.2 Hz, *Ph*), 124.6 (d, J_{C-H} = 157.1 Hz, *Ph*), 120.9 (d, J_{C-H} = 157.7 Hz, *Ph*), 89.9 (s, C_5Me$_5$), 84.7 (s, C_5Me$_5$), 66.3 (s, -*C*Ph), 12.8 (q, J_{C-H} = 126.4 Hz, C_5Me_5), 11.9 (q, J_{C-H} = 126.1 Hz, C_5Me_5). IR (ATR, cm^{-1}): 3061, 2974, 2903, 1587, 1475, 1369, 1304, 1071, 1025, 873, 755. Anal. Calcd for $C_{38}H_{54}Ru_3$: C, 56.07; H, 6.69. Found: C, 56.29; H, 6.76.

Preparation of {Cp*Ru(μ-H)}$_3$(μ_3-η^2:η^2(⊥)-^{t}BuCCH) (2b). A 50-mL flask was charged with THF (20 mL) and a triruthenium pentahydrido complex {Cp*Ru(μ-H)}$_3$(μ-H)$_2$ (**1**; 112 mg, 0.157 mmol). 3,3-dimethyl-1-butyne (23 μL, 0.190 mmol) was added with vigorous stirring. The solution was allowed to react for 1h at 25°C, and the color of the solution turned from dark-purple to dark-red. The solvent and remaining 3,3-dimethyl-1-butyne were then removed under reduced pressure, and 124 mg of **2b** was obtained as a reddish-brown solid (99% yield). ^{1}H NMR (400 MHz, toluene-d_8, -20ºC, TMS): δ 9.71 (s 1H, C*H*), 2.03 (s, 15H, C_5Me_5), 1.92 (s, 30H, C_5Me_5), 0.38 (s, 9H, C(CH_3)$_3$), -0.61 (s, 2H, Ru*H*), -23.46 (s, 1H, Ru*H*). ^{13}C NMR (100 MHz, benzene-d_6, 23.0ºC, TMS): δ 160.5 (d, J_{C-H} = 181.7 Hz, *C*H), 87.5 (s, C_5Me$_5$), 84.5 (s, C_5Me$_5$), 60.4 (s, *C*C(CH$_3$)$_3$), 34.4 (q, J_{C-H} = 124.5 Hz, C(*C*H$_3$)$_3$), 30.3 (s, *C*(CH$_3$)$_3$), 13.1 (q, J_{C-H} = 126.1 Hz, C_5Me_5), 12.7 (q, J_{C-H} = 126.1 Hz, C_5Me_5). IR (ATR, cm^{-1}): 2949, 2897, 1474, 1374, 1345, 1206, 1068, 1025, 886. Anal. Calcd for $C_{36}H_{58}Ru_3$: C, 54.45; H, 7.36. Found: C, 54.11; H, 7.63.

Preparation of {Cp*Ru(μ-H)}$_3$(μ_3-η^2:η^2(⊥)-PhCCMe) (2c). A 50-mL flask was charged with THF (20 mL) and a triruthenium pentahydrido complex {Cp*Ru(μ-H)}$_3$(μ-H)$_2$ (**1**; 172 mg, 0.241 mmol). 1-Pheny-1-propyne (75 μL, 0.599 mmol) was added with vigorous stirring. The solution was allowed to react for 20h at 25°C, and the color of the solution turned from

dark-purple to dark-green. The solvent was removed under reduced pressure. The residual solid was then dissolved in toluene (2mL) and purified by column chromatography on neutral alumina (Merck Art. No. 1097) with pentane/toluene. The first green-band including **2c** was collected. A 144 mg amount of **2c** was obtained as a dark-green solid on removal of the solvent under reduced pressure (72% yield). ^{1}H NMR (500 MHz, benzene-d_6, 23.0ºC, TMS): δ 7.07 (t, $J_{H\text{-}H}$ = 7.6 Hz, 2H, Ph-*meta*), 6.76 (t, $J_{H\text{-}H}$ = 7.6 Hz, 1H, Ph-*para*), 5.71 (d, $J_{H\text{-}H}$ = 7.6 Hz, 2H, Ph-*ortho*), 2.79 (s, -CCH_3), 1.89 (s, 30H, C_5Me_5), 1.70 (s, 15H, C_5Me_5), -8.41 (d, $J_{H\text{-}H}$ = 3.0 Hz, 2H, Ru*H*), -24.78 (t, $J_{H\text{-}H}$ = 3.0 Hz, 1H, Ru*H*). ^{13}C NMR (125 MHz, benzene-d_6, 23.0ºC, TMS): δ 181.1 (s, -*C*CH_3), 149.3 (s, *Ph-ipso*), 126.9 (d, $J_{C\text{-}H}$ = 156.0 Hz, *Ph*), 124.0 (d, $J_{C\text{-}H}$ = 155.6 Hz, *Ph*), 120.9 (d, $J_{C\text{-}H}$ = 157.6 Hz, *Ph*), 90.8 (s, $C_5$$Me_5$), 85.5 (s, $C_5$$Me_5$), 73.7 (s, -*C*Ph), 25.8 (q, $J_{C\text{-}H}$ = 125.8 Hz, -C*C*H_3), 12.2 (q, $J_{C\text{-}H}$ = 125.6 Hz, C_5Me_5), 11.9 (q, $J_{C\text{-}H}$ = 125.8 Hz, C_5Me_5). IR (ATR, cm^{-1}): 2976, 2962, 2903, 1586, 1477, 1368, 1262, 1098, 1024, 805. Anal. Calcd for $C_{39}H_{56}Ru_3$: C, 56.57; H, 6.82. Found: C, 56.82; H, 6.78.

Monitoring the reaction of 1 with phenylacetylene by means of NMR spectroscopy. An NMR tube equipped with a Teflon seal-cock was charged with **1** (10 mg, 15 μmol), benzene-d_6 (0.45 mL), and phenylacetylene (7 μL, 64 μmol) with cooling by dry-ice/methanol bath. Then, the NMR tube was degassed, and gradually warmed up to room temperature. After the solution was allowed to react for 2h at 25°C, the reaction solution was analyzed by means of NMR spectroscopy. Signals derived from **1** completely disappeared, and quantitative formation of **2a** was observed. In addition, signals arising from vinylic protons of styrene were observed at δ 6.58 (dd, $J_{H\text{-}H}$ = 17.6, 11.2 Hz), 5.60 (d, $J_{H\text{-}H}$ = 17.6 Hz), and 5.07 (d, $J_{H\text{-}H}$ = 11.2 Hz). The molar ratio between **2a** and styrene was estimated at 100:23 from the integral values. Trace amount of ethyl benzene was also observed.

Monitoring the reaction of 1 with 1-phenyl-1-propyne by means of NMR spectroscopy. An NMR tube equipped with a Teflon seal-cock was charged with **1** (13 mg, 18 μmol), benzene-d_6 (0.50 mL), and phenylacetylene (2 μL, 16 μmol) at room temperature. The solution was allowed to react for 18h at 25°C. The reaction solution was then analyzed by means of NMR spectroscopy, which showed 95% conversion of 1-phenyl-1-propyne as well as 52% conversion of **1**. The yield of **2c** was estimated at 48% on the basis of the intensity ratio of the Cp* signals. Formation of *cis*-1-phenyl-1-propene was also confirmed by the ^{1}H NMR signals appearing at δ 6.41 (d, $J_{H\text{-}H}$ = 13.2 Hz, 1H, Ph*H*C=CHMe) and 5.63 (m, 1H, PhHC=C*H*Me). The yield of *cis*-1-phenyl-1-propene was estimated at 45%.

Product analysis of the reaction of 1 with phenylacetylene by means of a gas chromatography. A 50-mL flask equipped with a septum rubber was charged with **1** (62 mg, 0.087 mmol), THF (3 mL), and benzene (84 mg, 1.07 mmol) as an internal standard. 3.970 g of the stock-solution of phenylacetylene in THF (7.7 mg/g; 0.30 mmol) was gradually added to the solution of **1** in 1.5h by using a microfeeder. After all of the stock-solution was added, the solution was allowed to react for 1h at 25°C, and then the solution was analyzed by means of gas chromatography. During the reaction, 0.10 mmol of phenylacetylene was consumed, and formation of styrene (0.023 mmol) and ethylbenzene (0.003 mmol) was observed.

Reaction of 2a with dihydrogen in a sealed NMR tube. An NMR tube equipped with a Teflon seal-cock was charged with **2a** (6.7 mg, 8.2 μmol) and benzene-d_6 (0.45 mL). After the solution was degassed, 1 atm of dihydrogen was introduced into the tube. The NMR tube was then heated at 70°C, and analyzed periodically by means of ^{1}H NMR spectroscopy. Results of the reaction are summarized in Table S-2.

Table S-2. Time-distribution of the reaction of **2a** with 1 atm of H_2 in a sealed NMR tube

Time (h)	Complexes (%)		Volatiles (%)	
	2a	**1**	**Styrene**	**Ethylbenzene**
0	100	0	0	0
17	65	35	8	27
33	47	53	14	39
77	13	87	0	87

Reaction of 2b with dihydrogen in a sealed NMR tube. An NMR tube equipped with a Teflon seal-cock was charged with **2a** (4.0 mg, 5.0 μmol) and benzene-d_6 (0.45 mL). After the solution was degassed, 1 atm of dihydrogen was introduced into the tube. The NMR tube was then heated at 70°C, and analyzed by means of ^{1}H NMR spectroscopy after 20h. All of **2b** was consumed, and formation of **1** with equimolar amount of neohexane (δ 1.18 (q, $J_{H\text{-}H}$ = 7.2 Hz, 2H, -CH_2-), 0.85 (s, 9H, -C(CH_3)$_3$), 0.81 (t, $J_{H\text{-}H}$ = 7.2 Hz, 3H, -CH_3) was observed.

Reaction of 2a with dihydrogen in a glass-autoclave. Complex **2a** (44.2 mg, 0.054 mmol) was dissolved in toluene-d_8 (2.5 mL) in a 20-mL flask. The reaction solution (0.5 ml) was then transferred to a 50-mL glass-autoclave by using a gas-tight syringe. 5 atm of dihydrogen was introduced in the glass-autoclave, and allowed to react at 90°C for 7h with vigorous stirring. After the solution was cooled at room temperature, dihydrogen was slowly released from the glass-autoclave. The reaction solution was then transferred to an NMR tube. 92% conversion of **2a** into **1** was observed by the ^{1}H NMR spectrum.

Reaction of 2c with dihydrogen in a glass-autoclave at 170°C. A 50-mL glass-autoclave was charged with **2c** (15.9 mg, 0.019 mmol) and toluene (2.0 mL). 5 atm of dihydrogen was introduced in the glass-autoclave, and allowed to react at 170°C for 24h with vigorous stirring.

After the solution was removed *in vacuo*, a residual solid was dissolved in benzene-d_6 (0.5 mL). The solution was then transferred to an NMR tube. 89% conversion of **2c** into **1** was observed by the ^{1}H NMR spectrum.

Reaction of 2c with dihydrogen in a glass-autoclave at 100°C. A 50-mL glass-autoclave was charged with **2c** (32.1 mg, 0.036 mmol) and toluene (5.0 mL). 5 atm of dihydrogen was introduced in the glass-autoclave, and allowed to react at 100°C for 72h with vigorous stirring. After the solution was removed *in vacuo*, a residual solid was dissolved in benzene-d_6 (0.5 mL). The solution was then transferred to an NMR tube. Formation of **1** was not observed, and all of **2c** remained unchanged.

Results of the X-ray diffraction studies of {Cp*Ru(μ-H)$_3$}(μ_3-η^2:η^2($\perp$)-PhCCH) (2a).

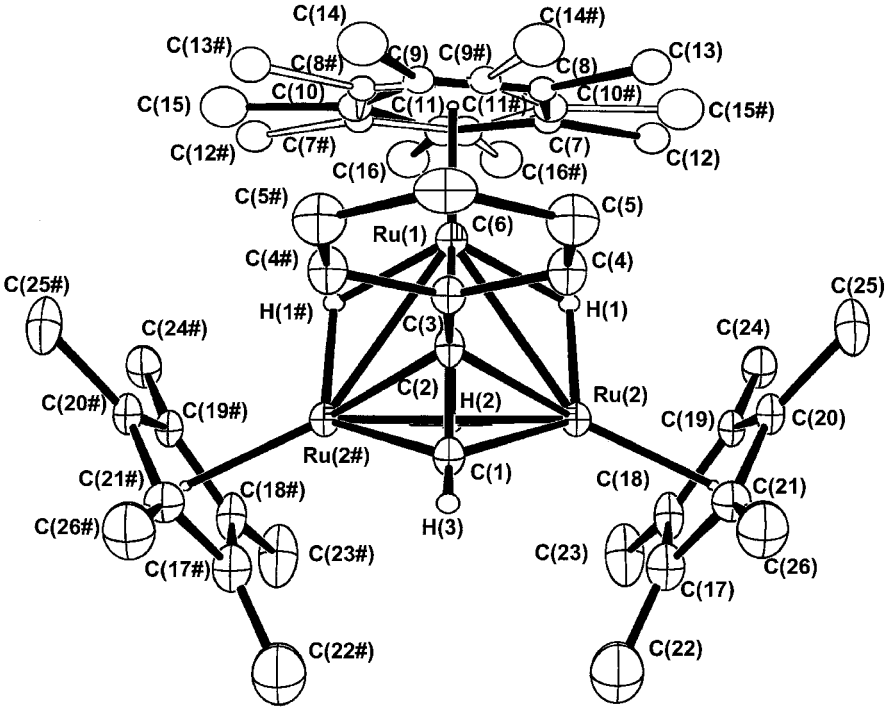

Table S-3. Crystal data and structure refinement for 2a.

Identification code,a
Empirical formula,C38 H54 Ru3
Formula weight,814.02
Temperature,153(2) K
Wavelength,0.71069 Å
Crystal system,Monoclinic
Space group,C2/m
Unit cell dimensions, a = 17.083(6)Å α = 90°
, b = 18.356(6)Å β = 105.732(15)°
, c = 11.473(4)Å γ = 90°
Volume, 3463(2) $Å^3$
Z, 4
Density (calculated), 1.561 Mg/m^3
Absorption coefficient, 1.316 mm^{-1}
F(000), 1656
Crystal size, 0.40 x 0.40 x 0.30 mm
Theta range for data collection, 3.33 to 30.03 °.
Index ranges,0<=h<=24; 0<=k<=25; -16<=l<=15
Reflections collected, 20349
Independent reflections, 5204 [R(int) = 5.8571]
Reflections observed (>2σ), 4191
Refinement method, Full-matrix least-squares on F^2
Data / restraints / parameters, 5186 / 0 / 206
Goodness-of-fit on F^2, 1.028
Final R indices [I>2s(I)],R_1 = 0.0468 wR_2 = 0.1166
R indices (all data), R_1 = 0.0607 wR_2 = 0.1252
Largest diff. peak and hole, 1.439 and -1.367 e.$Å^{-3}$

Table S-4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 2a.U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom, x, y, z, U(eq)

Ru(1),6543(1),5000,3108(1),22(1),
Ru(2),7641(1),5777(1),2173(1),21(1),
C(2),7853(4),5000,3736(5),24(1),
C(3),8171(3),5000,5076(5),23(1),
C(1),8405(4),5000,3041(5),25(1),
C(4),8339(3),5653(2),5720(4),32(1),
C(5),8674(3),5655(3),6975(4),40(1),
C(6),8843(4),5000,7600(6),36(1),
C(7),5407(2),5608(2),3098(3),22(1),
C(8),5895(2),5556(2),4322(3),23(1),
C(9),6011(3),4802(2),4625(4),28(2),
C(10),5596(3),4387(2),3588(4),35(2),
C(11),5222(3),4885(2),2645(4),31(2),
C(12),5134(4),6307(3),2402(5),42(2),
C(13),6230(4),6192(3),5154(5),38(2),
C(14),6492(4),4495(3),5836(5),62(3),
C(15),5557(5),3562(3),3504(6),74(4),
C(16),4718(4),4682(3),1382(5),59(3),
C(17),8471(3),6339(3),1315(5),39(1),
C(18),7664(3),6409(2),528(4),35(1),
C(19),7189(3),6801(2),1143(4),26(1),
C(20),7686(3),6964(2),2345(4),27(1),
C(21),8483(3),6686(2),2441(4),35(1),
C(22),9197(4),6029(4),989(8),73(2),
C(23),7388(6),6164(3),-766(5),68(2),
C(24),6334(3),7044(3),597(5),46(1),
C(25),7436(4),7420(3),3273(5),48(1),
C(26),9230(4),6784(3),3484(7),63(2),

Table S-5. Bond lengths [Å] and angles [°] for 2a.

Ru(1)-C(2),2.157(6)
Ru(1)-C(10)#1,2.161(4)
Ru(1)-C(10),2.161(5)
Ru(1)-C(11)#1,2.183(4)
Ru(1)-C(11),2.183(4)
Ru(1)-C(9)#1,2.201(4)
Ru(1)-C(9),2.201(4)
Ru(1)-C(7)#1,2.235(4)
Ru(1)-C(7),2.235(4)
Ru(1)-C(8)#1,2.246(5)
Ru(1)-C(8),2.246(4)
Ru(1)-Ru(2),2.7919(8)
Ru(2)-C(1),2.006(5)
Ru(2)-C(21),2.169(4)
Ru(2)-C(20),2.187(4)
Ru(2)-C(17),2.191(4)
Ru(2)-C(18),2.225(4)
Ru(2)-C(2),2.242(4)
Ru(2)-C(19),2.243(4)
Ru(2)-Ru(2)#1,2.8531(10)
C(2)-C(1),1.392(7)
C(2)-C(3),1.485(8)
C(2)-Ru(2)#1,2.242(4)
C(3)-C(4),1.396(5)
C(3)-C(4)#1,1.396(5)
C(1)-Ru(2)#1,2.006(5)
C(4)-C(5),1.397(6)
C(5)-C(6),1.390(6)
C(6)-C(5)#1,1.390(6)
C(7)-C(10)#1,0.5671
C(7)-C(11)#1,1.049(7)
C(7)-C(8),1.428(2)
C(7)-C(11),1.428(2)
C(7)-C(12),1.518(3)
C(7)-C(15)#1,1.593(7)
C(7)-C(9)#1,1.928(4)
C(8)-C(9)#1,0.745(6)
C(8)-C(10)#1,0.8642(14)
C(8)-C(9),1.428(2)
C(8)-C(13),1.518(3)
C(8)-C(14)#1,1.762(3)
C(8)-C(15)#1,1.881(6)
C(9)-C(9)#1,0.727(7)
C(9)-C(8)#1,0.745(6)
C(9)-C(10),1.428(2)
C(9)-C(14),1.518(3)
C(9)-C(14)#1,1.911(7)
C(9)-C(10)#1,1.917(5)
C(9)-C(13)#1,1.927(9)
C(9)-C(7)#1,1.928(4)
C(10)-C(7)#1,0.567(4)
C(10)-C(8)#1,0.864(2)
C(10)-C(11),1.428(2)
C(10)-C(15),1.518(3)
C(10)-C(11)#1,1.728(7)
C(10)-C(12)#1,1.876(6)
C(10)-C(9)#1,1.917(6)
C(11)-C(11)#1,0.421(8)
C(11)-C(7)#1,1.049(7)
C(11)-C(16),1.518(3)
C(11)-C(16)#1,1.672(6)
C(11)-C(10)#1,1.728(5)
C(12)-C(15)#1,1.2979(14)
C(12)-C(10)#1,1.876(6)
C(13)-C(14)#1,1.487(9)
C(13)-C(9)#1,1.927(7)
C(13)-C(15)#1,1.982(2)
C(14)-C(13)#1,1.487(8)
C(14)-C(8)#1,1.762(3)
C(14)-C(14)#1,1.854(10)
C(14)-C(9)#1,1.911(6)
C(15)-C(12)#1,1.298(4)
C(15)-C(7)#1,1.593(8)
C(15)-C(8)#1,1.881(9)
C(15)-C(13)#1,1.982(6)
C(16)-C(16)#1,1.166(11)
C(16)-C(11)#1,1.672(5)
C(17)-C(18),1.434(7)
C(17)-C(21),1.436(7)
C(17)-C(22),1.501(7)
C(18)-C(19),1.410(6)
C(18)-C(23),1.499(7)
C(19)-C(20),1.440(6)
C(19)-C(24),1.494(6)
C(20)-C(21),1.429(6)
C(20)-C(25),1.506(6)
C(21)-C(26),1.505(7)

C(2)-Ru(1)-C(10)#1,134.06(13)
C(2)-Ru(1)-C(10),134.06(15)
C(10)#1-Ru(1)-C(10),62.69(17)
C(2)-Ru(1)-C(11)#1,172.44(14)
C(10)#1-Ru(1)-C(11)#1,38.38(9)
C(10)-Ru(1)-C(11)#1,46.87(18)
C(2)-Ru(1)-C(11),172.44(14)
C(10)#1-Ru(1)-C(11),46.87(14)
C(10)-Ru(1)-C(11),38.38(8)
C(11)#1-Ru(1)-C(11),11.1(2)
C(2)-Ru(1)-C(9)#1,110.42(17)
C(10)#1-Ru(1)-C(9)#1,38.20(8)
C(10)-Ru(1)-C(9)#1,52.11(17)
C(11)#1-Ru(1)-C(9)#1,63.61(12)
C(11)-Ru(1)-C(9)#1,65.63(13)
C(2)-Ru(1)-C(9),110.42(18)
C(10)#1-Ru(1)-C(9),52.11(14)
C(10)-Ru(1)-C(9),38.20(8)
C(11)#1-Ru(1)-C(9),65.63(13)
C(11)-Ru(1)-C(9),63.61(12)
C(9)#1-Ru(1)-C(9),19.00(18)
C(2)-Ru(1)-C(7)#1,145.28(12)
C(10)#1-Ru(1)-C(7)#1,63.38(11)
C(10)-Ru(1)-C(7)#1,14.70(10)
C(11)#1-Ru(1)-C(7)#1,37.69(7)
C(11)-Ru(1)-C(7)#1,27.44(17)
C(9)#1-Ru(1)-C(7)#1,62.77(11)
C(9)-Ru(1)-C(7)#1,51.51(12)
C(2)-Ru(1)-C(7),145.28(12)
C(10)#1-Ru(1)-C(7),14.7
C(10)-Ru(1)-C(7),63.38(12)
C(11)#1-Ru(1)-C(7),27.44(17)
C(11)-Ru(1)-C(7),37.69(8)
C(9)#1-Ru(1)-C(7),51.51(12)
C(9)-Ru(1)-C(7),62.77(12)
C(7)#1-Ru(1)-C(7),59.87(19)
C(2)-Ru(1)-C(8)#1,115.71(17)
C(10)#1-Ru(1)-C(8)#1,63.20(12)
C(10)-Ru(1)-C(8)#1,22.51(7)
C(11)#1-Ru(1)-C(8)#1,62.87(13)

C(11)-Ru(1)-C(8)#1,57.07(11)
C(9)#1-Ru(1)-C(8)#1,37.44(10)
C(9)-Ru(1)-C(8)#1,19.26(16)
C(7)#1-Ru(1)-C(8)#1,37.16(12)
C(7)-Ru(1)-C(8)#1,69.92(14)
C(2)-Ru(1)-C(8),115.71(16)
C(10)#1-Ru(1)-C(8),22.5
C(10)-Ru(1)-C(8),63.20(12)
C(11)#1-Ru(1)-C(8),57.07(12)
C(11)-Ru(1)-C(8),62.87(12)
C(9)#1-Ru(1)-C(8),19.26(15)
C(9)-Ru(1)-C(8),37.44(8)
C(7)#1-Ru(1)-C(8),69.92(16)
C(7)-Ru(1)-C(8),37.16(7)
C(8)#1-Ru(1)-C(8),54.07(17)
C(2)-Ru(1)-Ru(2),51.98(11)
C(10)#1-Ru(1)-Ru(2),117.37(9)
C(10)-Ru(1)-Ru(2),172.48(12)
C(11)#1-Ru(1)-Ru(2),127.96(10)
C(11)-Ru(1)-Ru(2),135.53(11)
C(9)#1-Ru(1)-Ru(2),133.13(9)
C(9)-Ru(1)-Ru(2),148.48(10)
C(7)#1-Ru(1)-Ru(2),157.79(10)
C(7)-Ru(1)-Ru(2),114.57(10)
C(8)#1-Ru(1)-Ru(2),165.00(12)
C(8)-Ru(1)-Ru(2),120.10(9)
C(1)-Ru(2)-C(21),99.16(19)
C(1)-Ru(2)-C(20),131.41(18)
C(21)-Ru(2)-C(20),38.30(17)
C(1)-Ru(2)-C(17),98.3(2)
C(21)-Ru(2)-C(17),38.45(19)
C(20)-Ru(2)-C(17),63.88(16)
C(1)-Ru(2)-C(18),129.2(2)
C(21)-Ru(2)-C(18),63.64(18)
C(20)-Ru(2)-C(18),63.18(15)
C(17)-Ru(2)-C(18),37.88(19)
C(1)-Ru(2)-C(2),37.7(2)
C(21)-Ru(2)-C(2),114.77(18)
C(20)-Ru(2)-C(2),124.60(14)
C(17)-Ru(2)-C(2),132.5(2)
C(18)-Ru(2)-C(2),166.86(18)
C(1)-Ru(2)-C(19),160.37(19)
C(21)-Ru(2)-C(19),63.28(17)
C(20)-Ru(2)-C(19),37.92(15)
C(17)-Ru(2)-C(19),62.65(17)
C(18)-Ru(2)-C(19),36.78(16)
C(2)-Ru(2)-C(19),155.81(15)
C(1)-Ru(2)-Ru(1),82.01(15)
C(21)-Ru(2)-Ru(1),145.81(13)
C(20)-Ru(2)-Ru(1),119.05(11)
C(17)-Ru(2)-Ru(1),175.70(15)
C(18)-Ru(2)-Ru(1),139.50(14)
C(2)-Ru(2)-Ru(1),49.26(15)
C(19)-Ru(2)-Ru(1),117.35(11)
C(1)-Ru(2)-Ru(2)#1,44.68(13)
C(21)-Ru(2)-Ru(2)#1,140.27(13)
C(20)-Ru(2)-Ru(2)#1,175.00(11)
C(17)-Ru(2)-Ru(2)#1,118.10(12)
C(18)-Ru(2)-Ru(2)#1,121.40(11)
C(2)-Ru(2)-Ru(2)#1,50.49(9)
C(19)-Ru(2)-Ru(2)#1,146.93(10)
Ru(1)-Ru(2)-Ru(2)#1,59.272(13)
C(1)-C(2)-C(3),118.6(5)
C(1)-C(2)-Ru(1),127.7(4)
C(3)-C(2)-Ru(1),113.7(4)
C(1)-C(2)-Ru(2)#1,61.9(2)
C(3)-C(2)-Ru(2)#1,139.63(13)
Ru(1)-C(2)-Ru(2)#1,78.76(18)
C(1)-C(2)-Ru(2),61.9(2)
C(3)-C(2)-Ru(2),139.63(13)
Ru(1)-C(2)-Ru(2),78.76(18)
Ru(2)#1-C(2)-Ru(2),79.01(18)
C(4)-C(3)-C(4)#1,118.2(5)
C(4)-C(3)-C(2),120.9(3)
C(4)#1-C(3)-C(2),120.9(3)
C(2)-C(1)-Ru(2)#1,80.4(3)
C(2)-C(1)-Ru(2),80.4(3)
Ru(2)#1-C(1)-Ru(2),90.6(3)
C(3)-C(4)-C(5),121.1(4)
C(6)-C(5)-C(4),119.9(5)
C(5)-C(6)-C(5)#1,119.8(6)
C(10)#1-C(7)-C(11)#1,121.3(8)
C(10)#1-C(7)-C(8),4.8(6)
C(11)#1-C(7)-C(8),116.6(2)
C(10)#1-C(7)-C(11),112.7(7)
C(11)#1-C(7)-C(11),8.6(2)
C(8)-C(7)-C(11),108.0
C(10)#1-C(7)-C(12),121.3(7)
C(11)#1-C(7)-C(12),117.4(2)
C(8)-C(7)-C(12),126.0
C(11)-C(7)-C(12),126.0
C(10)#1-C(7)-C(15)#1,72.1(6)
C(11)#1-C(7)-C(15)#1,166.6(3)
C(8)-C(7)-C(15)#1,76.77(10)
C(11)-C(7)-C(15)#1,175.13(10)
C(12)-C(7)-C(15)#1,49.24(10)
C(10)#1-C(7)-C(9)#1,23.9(5)
C(11)#1-C(7)-C(9)#1,97.4(3)
C(8)-C(7)-C(9)#1,19.17(18)
C(11)-C(7)-C(9)#1,88.84(18)
C(12)-C(7)-C(9)#1,145.17(18)
C(15)#1-C(7)-C(9)#1,95.93(16)
C(10)#1-C(7)-Ru(1),75.2(4)
C(11)#1-C(7)-Ru(1),73.5(2)
C(8)-C(7)-Ru(1),71.84(14)
C(11)-C(7)-Ru(1),69.17(14)
C(12)-C(7)-Ru(1),124.59(14)
C(15)#1-C(7)-Ru(1),113.91(13)
C(9)#1-C(7)-Ru(1),63.33(16)
C(9)#1-C(8)-C(10)#1,124.9(6)
C(9)#1-C(8)-C(7),121.8(2)
C(10)#1-C(8)-C(7),3.2(4)
C(9)#1-C(8)-C(9),13.8(2)
C(10)#1-C(8)-C(9),111.1(4)
C(7)-C(8)-C(9),108.0
C(9)#1-C(8)-C(13),112.2(2)
C(10)#1-C(8)-C(13),122.9(4)
C(7)-C(8)-C(13),126.0
C(9)-C(8)-C(13),126.0
C(9)#1-C(8)-C(14)#1,58.89(15)
C(10)#1-C(8)-C(14)#1,176.0(6)
C(7)-C(8)-C(14)#1,179.2(3)
C(9)-C(8)-C(14)#1,72.7(3)
C(13)-C(8)-C(14)#1,53.3(3)
C(9)#1-C(8)-C(15)#1,177.2(3)
C(10)#1-C(8)-C(15)#1,52.5(3)
C(7)-C(8)-C(15)#1,55.57(15)
C(9)-C(8)-C(15)#1,163.54(15)
C(13)-C(8)-C(15)#1,70.44(15)
C(14)#1-C(8)-C(15)#1,123.7(4)

C(9)#1-C(8)-Ru(1),76.9(2)
C(10)#1-C(8)-Ru(1),73.2(3)
C(7)-C(8)-Ru(1),71.00(14)
C(9)-C(8)-Ru(1),69.56(14)
C(13)-C(8)-Ru(1),125.02(13)
C(14)#1-C(8)-Ru(1),109.6(2)
C(15)#1-C(8)-Ru(1),102.58(14)
C(9)#1-C(9)-C(8)#1,151.9(3)
C(9)#1-C(9)-C(8),14.2
C(8)#1-C(9)-C(8),137.7(3)
C(9)#1-C(9)-C(10),122.2
C(8)#1-C(9)-C(10),29.8(3)
C(8)-C(9)-C(10),108.0
C(9)#1-C(9)-C(14),111.8
C(8)#1-C(9)-C(14),96.3(3)
C(8)-C(9)-C(14),126.0
C(10)-C(9)-C(14),126.0
C(9)#1-C(9)-C(14)#1,47.5(2)
C(8)#1-C(9)-C(14)#1,160.5(4)
C(8)-C(9)-C(14)#1,61.7(2)
C(10)-C(9)-C(14)#1,169.7(2)
C(14)-C(9)-C(14)#1,64.3(2)
C(9)#1-C(9)-C(10)#1,39.08(13)
C(8)#1-C(9)-C(10)#1,112.9(3)
C(8)-C(9)-C(10)#1,24.88(12)
C(10)-C(9)-C(10)#1,83.12(13)
C(14)-C(9)-C(10)#1,150.88(12)
C(14)#1-C(9)-C(10)#1,86.6(3)
C(9)#1-C(9)-C(13)#1,161.19(11)
C(8)#1-C(9)-C(13)#1,46.9(4)
C(8)-C(9)-C(13)#1,175.35(11)
C(10)-C(9)-C(13)#1,76.61(11)
C(14)-C(9)-C(13)#1,49.40(11)
C(14)#1-C(9)-C(13)#1,113.67(19)
C(10)#1-C(9)-C(13)#1,159.72(18)
C(9)#1-C(9)-C(7)#1,113.0(2)
C(8)#1-C(9)-C(7)#1,39.0(2)
C(8)-C(9)-C(7)#1,98.8(2)
C(10)-C(9)-C(7)#1,9.3(2)
C(14)-C(9)-C(7)#1,135.2(2)
C(14)#1-C(9)-C(7)#1,160.5(3)
C(10)#1-C(9)-C(7)#1,73.88(14)
C(13)#1-C(9)-C(7)#1,85.8(3)
C(9)#1-C(9)-Ru(1),80.50(14)
C(8)#1-C(9)-Ru(1),83.79(16)
C(8)-C(9)-Ru(1),72.99(14)
C(10)-C(9)-Ru(1),69.40(14)
C(14)-C(9)-Ru(1),123.24(14)
C(14)#1-C(9)-Ru(1),106.0(2)
C(10)#1-C(9)-Ru(1),62.88(13)
C(13)#1-C(9)-Ru(1),108.60(17)
C(7)#1-C(9)-Ru(1),65.16(16)
C(7)#1-C(10)-C(8)#1,172.0(11)
C(7)#1-C(10)-C(11),38.9(7)
C(8)#1-C(10)-C(11),133.3(5)
C(7)#1-C(10)-C(9),146.9(7)
C(8)#1-C(10)-C(9),25.3(5)
C(11)-C(10)-C(9),108.0
C(7)#1-C(10)-C(15),87.1(7)
C(8)#1-C(10)-C(15),100.7(5)
C(11)-C(10)-C(15),126.0
C(9)-C(10)-C(15),126.0
C(7)#1-C(10)-C(11)#1,49.7(5)
C(8)#1-C(10)-C(11)#1,122.5(6)
C(11)-C(10)-C(11)#1,10.78(16)
C(9)-C(10)-C(11)#1,97.21(16)
C(15)-C(10)-C(11)#1,136.79(16)
C(7)#1-C(10)-C(12)#1,43.7(5)
C(8)#1-C(10)-C(12)#1,144.0(7)
C(11)-C(10)-C(12)#1,82.6(3)
C(9)-C(10)-C(12)#1,169.4(3)
C(15)-C(10)-C(12)#1,43.4(3)
C(11)#1-C(10)-C(12)#1,93.4(2)
C(7)#1-C(10)-C(9)#1,128.2(8)
C(8)#1-C(10)-C(9)#1,44.0(4)
C(11)-C(10)-C(9)#1,89.29(13)
C(9)-C(10)-C(9)#1,18.71(13)
C(15)-C(10)-C(9)#1,144.71(13)
C(11)#1-C(10)-C(9)#1,78.5(2)
C(12)#1-C(10)-C(9)#1,171.9(3)
C(7)#1-C(10)-Ru(1),90.1(6)
C(8)#1-C(10)-Ru(1),84.3(3)
C(11)-C(10)-Ru(1),71.63(15)
C(9)-C(10)-Ru(1),72.40(14)
C(15)-C(10)-Ru(1),121.68(13)
C(11)#1-C(10)-Ru(1),67.22(18)
C(12)#1-C(10)-Ru(1),111.41(15)
C(9)#1-C(10)-Ru(1),65.01(16)
C(11)#1-C(11)-C(7)#1,149.63(19)
C(11)#1-C(11)-C(7),21.8
C(7)#1-C(11)-C(7),127.83(19)
C(11)#1-C(11)-C(10),129.8
C(7)#1-C(11)-C(10),19.85(19)
C(7)-C(11)-C(10),108.0
C(11)#1-C(11)-C(16),104.2
C(7)#1-C(11)-C(16),106.16(19)
C(7)-C(11)-C(16),126.0
C(10)-C(11)-C(16),126.0
C(11)#1-C(11)-C(16)#1,61.7(3)
C(7)#1-C(11)-C(16)#1,148.7(4)
C(7)-C(11)-C(16)#1,83.5(3)
C(10)-C(11)-C(16)#1,168.5(3)
C(16)-C(11)-C(16)#1,42.5(3)
C(11)#1-C(11)-C(10)#1,39.42(14)
C(7)#1-C(11)-C(10)#1,110.22(15)
C(7)-C(11)-C(10)#1,17.63(14)
C(10)-C(11)-C(10)#1,90.38(14)
C(16)-C(11)-C(10)#1,143.62(14)
C(16)#1-C(11)-C(10)#1,101.1(4)
C(11)#1-C(11)-Ru(1),84.47(14)
C(7)#1-C(11)-Ru(1),79.05(17)
C(7)-C(11)-Ru(1),73.14(14)
C(10)-C(11)-Ru(1),69.99(15)
C(16)-C(11)-Ru(1),122.53(14)
C(16)#1-C(11)-Ru(1),114.9(2)
C(10)#1-C(11)-Ru(1),65.91(13)
C(15)#1-C(12)-C(7),68.4(4)
C(15)#1-C(12)-C(10)#1,53.4(3)
C(7)-C(12)-C(10)#1,14.97(15)
C(14)#1-C(13)-C(8),71.8(2)
C(14)#1-C(13)-C(9)#1,50.8(3)
C(8)-C(13)-C(9)#1,20.99(6)
C(14)#1-C(13)-C(15)#1,135.2(4)
C(8)-C(13)-C(15)#1,63.4(3)
C(9)#1-C(13)-C(15)#1,84.4(2)
C(13)#1-C(14)-C(9),79.8(2)
C(13)#1-C(14)-C(8)#1,54.92(9)
C(9)-C(14)-C(8)#1,24.9(3)
C(13)#1-C(14)-C(14)#1,148.0(2)
C(9)-C(14)-C(14)#1,68.2

C(8)#1-C(14)-C(14)#1,93.1(3)
C(13)#1-C(14)-C(9)#1,100.45(18)
C(9)-C(14)-C(9)#1,20.68(15)
C(8)#1-C(14)-C(9)#1,45.53(16)
C(14)#1-C(14)-C(9)#1,47.53(15)
C(12)#1-C(15)-C(10),83.2(5)
C(12)#1-C(15)-C(7)#1,62.4(5)
C(10)-C(15)-C(7)#1,20.82(11)
C(12)#1-C(15)-C(8)#1,110.0(6)
C(10)-C(15)-C(8)#1,26.84(12)
C(7)#1-C(15)-C(8)#1,47.7(2)
C(12)#1-C(15)-C(13)#1,156.1(8)
C(10)-C(15)-C(13)#1,73.0(3)
C(7)#1-C(15)-C(13)#1,93.8(4)
C(8)#1-C(15)-C(13)#1,46.2(2)
C(16)#1-C(16)-C(11),75.8
C(16)#1-C(16)-C(11)#1,61.7(2)
C(11)-C(16)-C(11)#1,14.1(2)
C(18)-C(17)-C(21),107.7(4)
C(18)-C(17)-C(22),126.5(6)
C(21)-C(17)-C(22),125.5(6)
C(18)-C(17)-Ru(2),72.3(3)
C(21)-C(17)-Ru(2),69.9(2)
C(22)-C(17)-Ru(2),127.7(3)
C(19)-C(18)-C(17),108.4(4)
C(19)-C(18)-C(23),125.4(5)
C(17)-C(18)-C(23),126.0(5)
C(19)-C(18)-Ru(2),72.3(2)
C(17)-C(18)-Ru(2),69.8(2)
C(23)-C(18)-Ru(2),127.6(3)
C(18)-C(19)-C(20),108.4(4)
C(18)-C(19)-C(24),124.9(4)
C(20)-C(19)-C(24),126.6(4)
C(18)-C(19)-Ru(2),70.9(2)
C(20)-C(19)-Ru(2),68.9(2)
C(24)-C(19)-Ru(2),129.0(3)
C(21)-C(20)-C(19),107.6(4)
C(21)-C(20)-C(25),126.2(5)
C(19)-C(20)-C(25),125.8(4)
C(21)-C(20)-Ru(2),70.2(2)
C(19)-C(20)-Ru(2),73.2(2)
C(25)-C(20)-Ru(2),127.5(3)
C(20)-C(21)-C(17),107.9(4)
C(20)-C(21)-C(26),127.1(5)
C(17)-C(21)-C(26),124.8(5)
C(20)-C(21)-Ru(2),71.5(2)
C(17)-C(21)-Ru(2),71.6(3)
C(26)-C(21)-Ru(2),126.3(3)

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+1,z

Table S-6. Anisotropic displacement parameters ($Å^2$ x 10^3) for 2a. The anisotropic displacement factor exponent takes the form: $-2\ p^2\ [\ h^2\ a^{*2}\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U$

Atom, U11, U22, U33, U23, U13, U12

Ru(1),25(1),22(1),24(1),0,14(1),0
Ru(2),26(1),18(1),21(1),1(1),12(1),0(1)
C(2),33(3),17(2),26(3),0,17(2),0
C(3),26(3),23(2),22(2),0,11(2),0
C(1),32(3),19(2),29(3),0,15(2),0
C(4),40(2),26(2),30(2),-3(2),10(2),1(2)
C(5),48(3),41(2),31(2),-11(2),9(2),4(2)
C(6),34(3),53(4),25(3),0,13(3),0
C(17),47(3),31(2),51(3),16(2),32(2),7(2)
C(18),61(3),22(2),27(2),6(2),21(2),1(2)
C(19),34(2),16(2),29(2),4(1),9(2),-2(2)
C(20),38(2),16(2),30(2),2(1),14(2),-2(2)
C(21),33(2),30(2),39(2),12(2),6(2),-10(2)
C(22),68(4),63(4),114(6),46(4),70(5),28(3)
C(23),146(8),37(3),25(2),0(2),32(3),7(4)
C(24),38(3),30(2),60(3),9(2),-3(2),1(2)
C(25),90(5),25(2),36(2),-11(2),28(3),-7(2)
C(26),49(3),50(3),73(4),24(3),-14(3),-26(3)

Table S-7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 2a.

Atom, x, y, z, U(eq)

H(22A),9480,6419,683,100(30)
H(22B),9018,5656,363,210(70)
H(22C),9567,5810,1709,100(30)
H(23A),7684,5722,-869,70(20)
H(23B),7495,6549,-1293,100(30)
H(23C),6803,6061,-981,160(50)
H(24A),6107,7235,1233,100(30)
H(24B),6007,6630,199,100(30)
H(24C),6327,7427,-2,44(15)
H(25A),6856,7347,3195,200(60)
H(25B),7535,7936,3141,70(20)
H(25C),7753,7276,4086,53(17)
H(26A),9583,6357,3545,2000(1900)
H(26B),9069,6839,4237,55(19)
H(26C),9524,7220,3350,90(20)
H(1),6680(40),5750(30),2410(60),51(17)
H(2),7170(70),5000,1240(100),90(40)
H(3),8970(50),5000,3300(60),30(18)
H(4),8210(40),6150(40),5400(60),80(20)
H(5),8790(40),6160(30),7400(50),50(16)
H(6),9100(40),5000,8530(60),29(17)