Supporting Information

Ruthenium Promoted *Z*-Selective Head-to-Head Dimerization of Terminal Alkynes in Organic and Aqueous Medium

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Experimental section:

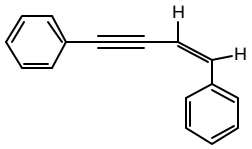
All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. The ligand $N(CH_2CH_2PPh_2)_3$ (NP_3)[1] and the complex of $RuCl_2(NP_3)$[2] were prepared according to literature methods. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 1600 series FT-IR spectrometer between KBr plates. ^1H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 with downfield values taken as positive. Mass Spectra were collected on a Finnigan TSQ 7000 Spectrometer. Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ).

$RuHCl(NP_3)$ (2). A C_2H_5OH (10 mL) solution of $NaBH_4$ (0.25 g, 6.6 mmol) was added to a THF solution of $RuCl_2(NP_3)$ (0.50 g, 0.61 mmol). The mixture was stirred for 2 h at 40-50 °C. After cooling, the solvents were removed completely under vacuum to give a yellow solid. The crude product was extracted with dichloromethane (3×10 mL). The solvent was removed again and the residue was washed with MeOH, and dried to give pure $RuHCl(NP_3)$ as yellow powders. Yield: 0.42 g, 87 %. IR: ν(Ru-H) 1882 cm^{-1} (vs). ^1H NMR (CD_2C1_2, 300 MHz): δ -6.56 (dt, J(PH) = 96.6, 25.5 Hz, 1H, RuH), 2.11-2.54 (m, 10H, CH_2), 2.74-2.83 (m, 2H, CH_2), 6.74-6.89 (m, 12H), 7.18-7.36 (m, 14H), 8.31 (m, 4H). ^{31}P NMR (CD_2C1_2): δ 28.5 (t, J(PP) = 43.1 Hz), 41.6 (d, J(PP) = 43.1 Hz). Anal. Calcd for $C_{42}H_{43}ClNP_3Ru$: C, 63.76; H, 5.48; N, 1.77. Found: C, 63.56; H, 5.30; N, 1.96.

$[RuH(CH_3CN)(NP_3)]OTf$ (3). A mixture of $RuHCl(NP_3)$ (0.40 g, 0.51 mmol) and TlOTf (0.500 g, 1.41 mmol) in acetonitrile (20 mL) was refluxed for 16 h to give a yellow solution and a white precipitate. After cooling, the white precipitate (TlCl) was removed by filtration through Celite. The solvent was removed under vacuum to give a yellow solid, which was purified by extraction with dichloromethane and removing the dichloromethane under vacuum. Yield: 0.41 g, 85%. IR: ν(Ru-H) 1886 cm^{-1} (s), ν(C≡N) 2256 (m). ^1H NMR (CD_2C1_2, 300 MHz): δ -6.92 (dt, J(PH) = 90.0, 24.0 Hz, 1H, RuH), 2.29 (s, 3H, CH_3), 2.57-3.08 (m, 12H, CH_2), 6.81-7.11 (m, 20H), 7.42-7.43 (m, 6H), 7.93-7.94 (m, 4H). ^{31}P NMR (CD_2C1_2): δ 28.5 (t, J(PP) = 43.1 Hz), 41.6(d, J(PP) = 43.1 Hz). Anal. Calcd for $C_{46}H_{48}Cl_2F_3N_2P_3O_3RuS$ ({[$RuH(CH_3CN)(NP_3)$]CF_3SO_3}CH_2Cl_2): C, 53.60; H, 4.69; N, 2.72. Found: C, 54.00; H, 4.95; N, 2.75. [Note: If the reaction mixture was refluxed for only 3 h, the ^{31}P NMR and ^1H NMR spectra indicate that the product contains another isomer. Selected NMR data of the other isomer are as follows. ^{31}P NMR: 49.9 (d, J(PP = 82.5 Hz), 61.9 (t, J(PP = 82.5 Hz). ^1H NMR (CD_2C1_2, 300 MHz): δ -13.50 (dt, J(PH) = 21.0,18.0 Hz, RuH)).

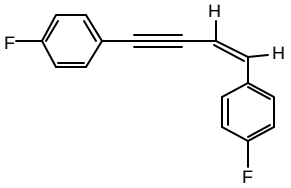
General procedure of dimerization of terminal alkynes catalyzed by the ruthenium complex $[RuH(CH_3CN)(NP_3)]OTf$. A mixture of a terminal alkyne and $[RuH(CH_3CN)(NP_3)]OTf$ (molar ratio: 100:0.03 ~ 2) in a solvent (such as toluene, isopropanol or H_2O) was refluxed for a period of time. After cooling, the solvent was removed and the crude product was purified by silica gel column chromatography.

Synthesis and characterization of (*Z*)-PhCH=CHC º CPh



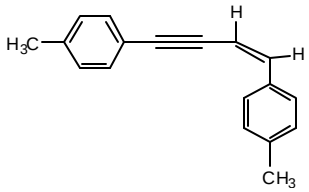
(a) Phenylacetylene (0.58 mL, 0.54 g, 5.28 mmol), catalyst (25 mg, 0.026 mmol), solvent (15 mL toluene), yield, 0.50 g (92 %).
(b) Phenylacetylene (0.56 mL, 0.52 g, 5.1 mmol), catalyst (24 mg, 0.025 mmol), solvent (15 mL water), yield, 0.45 g (86 %).
(c) Phenylacetylene (0.63 mL, 0.59 g, 5.8 mmol), catalyst (27 mg, 0.029 mmol), solvent (no), yield, 0.56 g (95 %).
(d) Phenylacetylene (3.0 mL, 2.8 g, 27.4 mmol), catalyst (8 mg, 0.0084 mmol), solvent (no), yield, 2.5 g (89 %).
^{1}H NMR ($CDCl_3$): δ 5.98 (d, J = 12.0 Hz, 1H), 6.75 (d, J = 12.0 Hz, 1H), 7.34 -7.49 (m, 8H), 7.54-7.57 (m, 2H), 7.99 (d, J = 7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 88.92, 96.53, 108.04, 124.10, 128.97, 129.03, 129.07, 129.17, 129.42, 132.11, 137.20, 139.33.

Synthesis and characterization of (*Z*)-(*p*-FC_6H_4)CH=CHC º C(*p*-FC_6H_4)



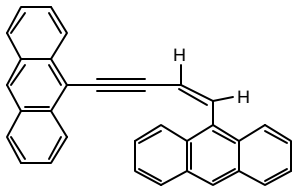
1-Ethynyl-4-fluorobenzene (0.32 g, 2.66 mmol), catalyst (25 mg, 0.026 mmol), solvent (15 mL toluene), yield, 0.26 g (81 %).
^{1}H NMR ($CDCl_3$): δ = 5.90 (d, J = 11.9 Hz, 1H), 6.68 (d, J = 11.9 Hz, 1H), 7.09 (m, 4H) 7.48 (dd, J = 8.5, 5.5 Hz, 2H), 7.92 (dd, 2H, J = 8.5, 5.6 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 88.33, 95.38, 107.50 (d, J(CF) = 6.9 Hz), 115.92 (d, J(CF) = 85.5 Hz), 116.45 (d, J(CF) = 88.2 Hz), 120.08 (d, J(CF) = 14.4 Hz), 131.16 (d, J(CF) = 32.4 Hz), 133.44 (d, J (CF)= 13.2 Hz), 133.98 (d, J(CF) = 33.3 Hz), 138.09, 161.59 (d, J(CF) = 20.4 Hz), 164.76 (d, J(CF) = 24.3 Hz).

Synthesis and characterization of (*Z*)-(*p*-MeC_6H_4)CH=CHC º C(*p*-MeC_6H_4)



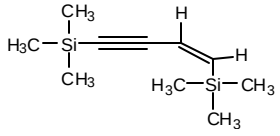
4-Ethynyltoluene (0.62 g, 5.33 mmol), catalyst (50mg, 0.053 mmol), solvent (15 mL toluene), yield, 0.53 g (85 %).
^{1}H NMR ($CDCl_3$): δ = 2.41 (s, 3H), 2.42 (s, 3H), 5.91 (d, J = 11.9 Hz, 1H), 6.70 (d, J = 11.9 Hz, 1H), 7.20 (d, J = 7.9 Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 7.45 (d, J = 7.9 Hz, 2H), 7.90 (d, J = 7.9 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 22.03, 22.15, 88.59, 96.58, 107.12, 121.20, 129.36, 129.63, 129.83, 131.95, 134.63, 138.89, 139.09 (2C).

Synthesis and characterization of (*Z*)-AnCH=CHCºCAn



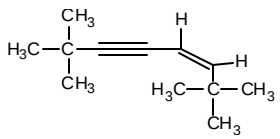
Anthrylacetylene (0.40 g, 1.98 mmol), catalyst (19 mg, 0.020 mmol), solvent (15 mL toluene), yield, 0.31 g (78 %).
^{1}H NMR ($CDCl_3$): δ = 6.78 (d, J = 11.3 Hz, 1H), 7.10 (m, 2H), 7.16-7.27 (m, 4H), 7.37-7.42 (m, 4H), 7.64 (d, J = 11.3Hz, 1H), 7.68 (d, 2H), 7.98-8.02 (m, 2H), 8.08 (s, 1H), 8.25- 8.28 (m, 2H), 8.47 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 92.62, 98.96, 116.52, 117.57, 126.05, 126.08, 126.55, 126.86, 126.99, 127.11, 127.79, 128.30, 128.93, 129.30, 130.14, 131.49, 132.25, 132.34, 133.12, 138.10. EI-MS: 404 $[M]^+$.

Synthesis and characterization of (*Z*)-Me_3SiCH=CHCºCSiMe_3



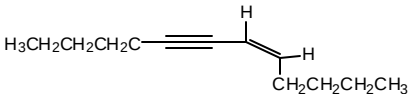
Trimethylsilylacetylene (0.75 mL, 0.52 g, 5.29 mmol), catalyst (50 mg, 0.053 mmol), solvent (20 mL benzene), yield, 0.46 g (88 %).
^{1}H NMR (C_6D_6): δ 0.19 (s, 18H), 6.17 (d, J = 15.0 Hz, 1H), 6.26 (d, J = 15.0 Hz, 1H).
^{13}C NMR (C_6D_6): δ - 0.44, 0.39, 99.24, 105.80, 125.32, 146.78.

Synthesis and characterization of (*Z*)-Me_3CCH=CHCºCCMe_3



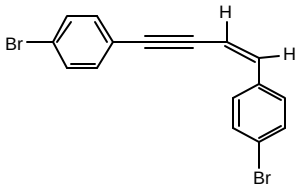
t-Butylacetylene (0.13 mL, 87 mg, 1.06 mmol), catalyst (10 mg, 0.011 mmol), solvent (0.5 mL benzene-d_6), conversion > 95 % (determined in situ by ^{1}H NMR).
^{1}H NMR (benzene-d_6): δ 1.43 (s, 9H), 1.48 (s, 9H), 5.69 (d, J = 11.9 Hz, 1H), 5.80 (d, J = 11.9 Hz, 1H). ^{13}C NMR (benzene-d_6): δ 29.02, 30.69, 31.53, 34.85, 78.30, 104.66, 108.55, 151.61.

Synthesis and characterization of (*Z*)-Me(CH$_2$)$_3$CH=CHC≡C(CH$_2$)$_3$Me



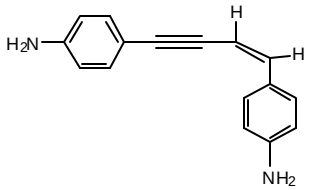
1-Hexyne (0.57 mL, 0.41g, 5.00 mmol), catalyst (24 mg, 0.025 mmol), solvent (15 mL toluene), yield, 0.13 g (32 %).
^{1}H NMR ($CDCl_3$): δ 0.89-0.94 (m, 6H), 1.33-1.50 (m, 8H), 2.28-2.36 (m, 4H), 5.43 (d, 1H, J = 10.6 Hz, 1H), 5.80 (dt, J = 10.6, 7.4 Hz, 1H). [small signals at 5.12 (br s, 0.04 H), and 5.20 (br s, 0.04 H) ppm assignable to *CH*$_2$=C(CH$_2$)$_3$Me)C≡C(CH$_2$)$_3$Me) could be seen]. ^{13}C NMR ($CDCl_3$): δ 14.28, 14.58, 19.89, 22.63, 22.96, 30.39, 31.65, 31.74, 78.04, 95.05, 109.99, 143.26.

Synthesis and characterization of (*Z*)-(*p*-BrC$_6$H$_4$)CH=CHC≡C(*p*-BrC$_6$H$_4$)



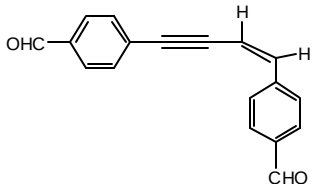
1-Ethynyl-4-bromobenzene (0.21 g, 1.16 mmol), catalyst (5.5 mg, 0.0058 mmol), solvent (10 mL toluene), yield, 0.19 g (90 %).
^{1}H NMR ($CDCl_3$): δ = 5.92 (d, J = 11.9 Hz, 1H), 6.66 (d, J = 11.9 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2 H).
^{13}C NMR ($CDCl_3$): δ 89.62, 96.08, 108.56, 122.74, 123.16, 123.54, 130.82, 132.12, 132.41, 133.45, 135.92, 138.40.

Synthesis and characterization of (*Z*)-(*p*-H$_2$NC$_6$H$_4$)CH=CHC≡C(*p*-H$_2$NC$_6$H$_4$)



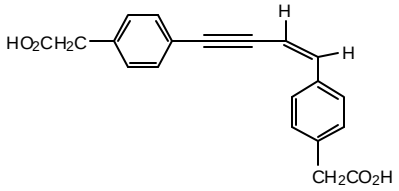
(a) 4-Ethynylaniline (0.62 g, 5.29 mmol), catalyst (50 mg, 0.053 mmol), solvent (15 mL toluene), yield, 0.54 g (87 %).
(b) 4-Ethynylaniline (0.62 g, 5.29 mmol), catalyst (25 mg, 0.026 mmol), solvent (20 mL water), yield, 0.53 g (85 %).
^{1}H NMR ($CDCl_3$): δ 3.80 (br, 4H, NH_2), 5.70 (d, J = 11.8 Hz, 1H), 6.52 (d, J = 11.8 Hz, 1H), 6.62 (d, J = 8.4 Hz, 2H), 6.67 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 87.82, 96.63, 104.33, 113.80, 115.17, 115.43, 128.39, 130.77, 133.30, 137.89, 147.22, 147.24. CI-MS: 235 $[M+1]^+$.

Synthesis and characterization of (*Z*)-(*p*-HOCC$_6$H$_4$)CH=CHº C(*p*-HOCC$_6$H$_4$)



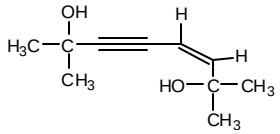
4-Ethynylbenzaldehyde (0.37 g, 2.84 mmol), catalyst (13 mg, 0.014 mmol), solvent (15 mL toluene), yield, 0.32 g (86 %).
^{1}H NMR (toluene-d$_8$): δ = 5.97 (d, J = 11.9 Hz, 1H), 6.52 (d, J = 11.9 Hz, 1H), 7.48 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 8.1 Hz, 2H), 7.77 (d, J = 8.1 Hz, 2H), 7.94 (d, J = 8.1 Hz, 2H), 9.75 (s, 1H), 9.85 (s, 1H). [small signals at 6.37 (d, 0.03H, J = 16.2Hz) and 6.99 (d, 0.03H, J = 16.2Hz) ppm assignable to (E)-(*p*-HOCC$_6$H$_4$)C*H*=C*H*C≡C(*p*-HOCC$_6$H$_4$) could also be seen]. ^{13}C NMR (toluene-d$_8$): δ = 92.37, 97.52, 110.70, 129.60, 130.24, 130.45, 130.52, 132.90, 137.26, 137.62, 139.75, 142.58, 191.00, 191.25. CI-MS: 261 $[M+1]^+$.

Synthesis and characterization of (*Z*)-(*p*-HO$_2$CCH$_2$C$_6$H$_4$)CH=CHº C(*p*-HO$_2$CH$_2$CC$_6$H$_4$)



4-Ethynylphenylacetic acid (0.30 g (1.87 mmol), catalyst (35 mg, 0.037 mmol), solvent, (20 mL isopropanol), yield, 0.22 g (73 %).
^{1}H NMR (CD$_3$CO$_2$D): δ 3.77 (s, 4H), 5.99 (d, J = 12.0 Hz, 1H), 6.79 (d, 1H, 1H), 7.37 (2H, J = 7.9 Hz, 2H), 7.43 (d, J = 7.9 Hz, 2H), 7.53 (d, 2H, J = 7.9 Hz, 2H), 7.98 (d, 2H, J = 7.9 Hz, 2H), 11.59 (br s, CO$_2$H). ^{13}C NMR (CD$_3$CO$_2$D): δ 42.41, 42.44, 90.33, 97.66, 109.21, 124.41, 130.98, 131.54, 131.83, 133.55, 136.44, 136.61, 137.79, 140.39, 178.76, 179.08. CI-MS: 321 $[M+1]^+$.

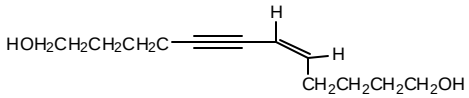
Synthesis and characterization of (*Z*)-Me$_2$C(OH)CH=CHº CC(OH)Me$_2$



2-Methyl-3-butyn-2-ol, 0.52 mL (0.45g, 5.35 mmol), catalyst (50 mg (0.053 mmol), solvent (15 mL toluene), yield, 0.41 g (91 %).

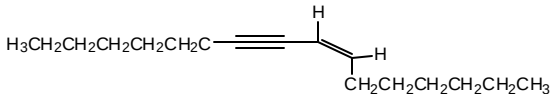
^{1}H NMR ($CDCl_3$): δ = 1.38 (s, 6H), 1.50 (s, 6H), 3.38 (br, 2H), 5.44 (d, J = 11.8 Hz, 1H), 5.94 (d, J =11.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 30.32, 31.69, 65.91, 72.97, 78.89, 102.19, 106.77, 150.46 ppm. CI-MS: 151 $[M+1-18]^+$.

Synthesis and characterization of (*Z*)-HO$(CH_2)_4$CH=CHC≡C$(CH_2)_4$OH



5-Hexyn-1-ol (0.29 mL, 0.26g, 2.6 mmol), catalyst (50 mg, 0.053 mmol), solvent (25 mL toluene), yield, 0.20 g (77 %).
5-Hexyn-1-ol (0.29 mL, 0.26g, 2.6 mmol), catalyst (25 mg, 0.027 mmol), solvent (15 mL water), conversion: 64 %, calculated from ^{1}H-NMR integration.
^{1}H NMR ($CDCl_3$): δ 1.18-1.62 (m, 8H), 2.24-2.32 (m, 4H), 3.36-3.57 (m, 6H), 5.36 (d, J = 10.6 Hz, 1H), 5.74 (dt, J = 10.6, 7.4 Hz, 1H). [small signals at 5.07 (br s, 0.04H) and 5.13 (br s, 0.04H) ppm assignable to C*H*$_2$=C($(CH_2)_4$OH)C≡C$(CH_2)_4$OH could also be seen]. ^{13}C NMR ($CDCl_3$): δ19.81, 25.45, 25.59, 30.14, 32.40, 32.58, 62.49, 62.62, 78.27, 94.65, 110.25, 142.74 ppm. CI-MS: 197 $[M+1]^+$.

Synthesis and characterization of (*Z*)-Me$(CH_2)_5$CH=CHC≡C$(CH_2)_5$Me



1-Octyne (3 mL, 2.2 g, 20.0 mmol), catalyst (46 mg, 0.049 mmol), solvent (no), yield, 1.89 g (86 %).
1-Octyne (0.78 mL, 0.58 g, 5.3 mmol), catalyst (25 mg, 0.026 mmol), solvent (15 mL water), yield, 0.49 g (84 %).
^{1}H NMR ($CDCl_3$): δ 0.87-0.90 (m, 6H), 1.29-1.44 (m, 14 H), 1.51-1.56 (m, 2H), 2.30-2.36 (m, 4H), 5.43 (d, J= 10.7 Hz, 1H), 5.80 (dt, J = 10.7, 7.4Hz, 1H). [small signals at 5.11 (br s 0.05H) and 5.20 (br s, 0.05H) ppm assignable to C*H*$_2$=C($(CH_2)_5$Me)C≡C$(CH_2)_5$Me could also be seen]. ^{13}C NMR ($CDCl_3$): δ = 14.71, 14.75, 20.23, 23.28, 23.32, 29.26, 29.46, 29.59($2CH_2$), 30.72, 32.08, 38.31, 78.11, 95.09, 110.04, 143.23 ppm.

References.

1. Sacconi, L.; Bertini, I. *J. Am. Chem. Soc.* **1968**, *90*, 5443
2. Dahlenburg, L.; Frosin, K. M.; Kerstan, S.; Werner, D. *J. Organomet. Chem.* **1991**, *407*, 115.

Table S1. Crystal data and structure refinement for **3**.

Empirical formula	C47H50Cl4 F3N2O3 P3RuS	
Formula weight	1115.73	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 23.587(5) Å	α= 90°.
	b = 16.031(3) Å	β= 104.843(4)°.
	c = 26.653(5) Å	γ = 90°.
Volume	9742(3) $Å^3$	
Z	8	
Density (calculated)	1.521 Mg/m^3	
Absorption coefficient	0.737 mm^{-1}	
F(000)	4560	
Crystal size	0.40 x 0.20 x 0.08 mm^3	
Theta range for data collection	1.34 to 25.00°.	
Index ranges	-28<=h<=21, -17<=k<=19, -31<=l<=31	
Reflections collected	49792	
Independent reflections	16980 [R(int) = 0.0774]	
Completeness to theta = 25.00°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.80	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16980 / 4 / 1172	
Goodness-of-fit on F^2	0.984	
Final R indices [I>2sigma(I)]	R1 = 0.0543, wR2 = 0.1145	
R indices (all data)	R1 = 0.1052, wR2 = 0.1271	
Largest diff. peak and hole	1.037 and -0.902 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1A)	2478(1)	1799(1)	3926(1)	16(1)
P(1A)	3420(1)	1418(1)	4319(1)	18(1)
P(2A)	2591(1)	3150(1)	3635(1)	17(1)
P(3A)	1492(1)	1696(1)	3870(1)	21(1)
N(1A)	2429(2)	1202(2)	3247(2)	19(1)
N(2A)	2511(2)	2414(2)	4658(1)	17(1)
C(1A)	2394(2)	825(3)	2886(2)	24(1)
C(2A)	2337(3)	312(4)	2424(2)	41(2)
C(11A)	3091(2)	2336(3)	5049(2)	24(1)
C(12A)	3393(2)	1510(3)	5000(2)	20(1)
C(13A)	2390(2)	3336(3)	4586(2)	24(1)
C(14A)	2746(2)	3730(3)	4248(2)	23(1)
C(15A)	2053(2)	2039(3)	4891(2)	24(1)
C(16A)	1445(2)	2030(3)	4522(2)	26(1)
C(21A)	3660(2)	339(3)	4259(2)	20(1)
C(22A)	3262(2)	-262(3)	4027(2)	22(1)
C(23A)	3435(2)	-1089(3)	3995(2)	28(1)
C(24A)	4004(2)	-1308(3)	4196(2)	28(1)
C(25A)	4413(2)	-701(3)	4419(2)	27(1)
C(26A)	4243(2)	111(3)	4448(2)	26(1)
C(31A)	4085(2)	1973(3)	4285(2)	22(1)
C(32A)	4479(2)	2344(3)	4698(2)	28(1)
C(33A)	4979(2)	2717(3)	4625(2)	33(1)
C(34A)	5090(2)	2755(3)	4145(2)	32(1)
C(35A)	4695(2)	2404(3)	3726(2)	29(1)
C(36A)	4200(2)	2014(3)	3796(2)	22(1)
C(41A)	3184(2)	3450(3)	3339(2)	22(1)
C(42A)	3606(2)	4042(3)	3549(2)	24(1)
C(43A)	4025(2)	4266(3)	3298(2)	28(1)
C(44A)	4032(2)	3911(3)	2827(2)	31(1)
C(45A)	3619(2)	3312(3)	2615(2)	29(1)
C(46A)	3201(2)	3082(3)	2866(2)	24(1)

C(51A)	1988(2)	3713(3)	3200(2)	19(1)
C(52A)	1822(2)	4510(3)	3294(2)	29(1)
C(53A)	1397(3)	4926(3)	2928(2)	37(2)
C(54A)	1143(2)	4558(3)	2460(2)	33(1)
C(55A)	1301(2)	3758(3)	2358(2)	27(1)
C(56A)	1716(2)	3340(3)	2730(2)	23(1)
C(61A)	909(2)	2277(3)	3425(2)	24(1)
C(62A)	775(2)	3100(3)	3522(2)	28(1)
C(63A)	353(3)	3546(4)	3165(2)	39(2)
C(64A)	68(2)	3173(4)	2697(2)	38(2)
C(65A)	206(3)	2372(4)	2591(2)	39(2)
C(66A)	624(2)	1928(4)	2953(2)	30(1)
C(71A)	1162(2)	652(3)	3802(2)	22(1)
C(72A)	607(2)	548(3)	3888(2)	30(1)
C(73A)	360(3)	-240(4)	3853(2)	39(2)
C(74A)	646(3)	-917(4)	3741(2)	38(2)
C(75A)	1192(3)	-823(4)	3646(2)	35(2)
C(76A)	1449(3)	-38(3)	3675(2)	28(1)
Ru(1B)	7264(1)	678(1)	3821(1)	15(1)
P(1B)	8201(1)	697(1)	4350(1)	19(1)
P(2B)	7250(1)	2078(1)	3586(1)	17(1)
P(3B)	6282(1)	366(1)	3536(1)	18(1)
N(1B)	7505(2)	163(2)	3213(2)	17(1)
N(2B)	7031(2)	1143(2)	4505(2)	20(1)
C(1B)	7670(2)	-167(3)	2903(2)	18(1)
C(2B)	7891(2)	-629(3)	2516(2)	32(1)
C(11B)	7447(2)	780(3)	4980(2)	28(1)
C(12B)	8077(2)	946(4)	4986(2)	26(1)
C(13B)	7002(2)	2084(3)	4540(2)	23(1)
C(14B)	7355(2)	2550(3)	4230(2)	22(1)
C(15B)	6434(2)	825(3)	4530(2)	19(1)
C(16B)	5993(2)	918(3)	4016(2)	24(1)
C(21B)	8629(2)	-275(3)	4416(2)	23(1)
C(22B)	8427(2)	-956(3)	4117(2)	25(1)
C(23B)	8770(3)	-1667(4)	4141(2)	34(1)
C(24B)	9322(2)	-1692(4)	4480(2)	33(1)

C(25B)	9522(2)	-1020(4)	4798(2)	31(1)
C(26B)	9180(2)	-311(3)	4767(2)	28(1)
C(31B)	8773(2)	1445(3)	4298(2)	24(1)
C(32B)	8970(2)	1412(3)	3845(2)	27(1)
C(33B)	9383(2)	1976(4)	3764(2)	34(1)
C(34B)	9601(3)	2568(4)	4125(2)	40(2)
C(35B)	9425(2)	2606(3)	4571(2)	35(2)
C(36B)	9012(2)	2048(3)	4661(2)	31(1)
C(41B)	7801(2)	2570(3)	3315(2)	20(1)
C(42B)	8091(2)	3304(3)	3511(2)	25(1)
C(43B)	8481(2)	3680(4)	3272(2)	31(1)
C(44B)	8575(2)	3345(4)	2830(2)	36(2)
C(45B)	8300(2)	2622(3)	2630(2)	31(1)
C(46B)	7917(2)	2230(3)	2870(2)	29(1)
C(51B)	6584(2)	2576(3)	3188(2)	22(1)
C(52B)	6222(2)	3091(3)	3382(2)	29(1)
C(53B)	5716(2)	3412(3)	3067(2)	33(1)
C(54B)	5578(3)	3253(4)	2547(2)	37(2)
C(55B)	5933(3)	2755(4)	2338(2)	36(2)
C(56B)	6434(2)	2397(3)	2655(2)	27(1)
C(61B)	5801(2)	637(3)	2911(2)	22(1)
C(62B)	5256(2)	1004(3)	2848(2)	28(1)
C(63B)	4900(2)	1189(3)	2360(2)	34(2)
C(64B)	5092(3)	990(4)	1929(2)	39(2)
C(65B)	5630(3)	630(3)	1979(2)	36(1)
C(66B)	5987(2)	451(3)	2461(2)	29(1)
C(71B)	6055(2)	-713(3)	3591(2)	19(1)
C(72B)	5500(2)	-914(3)	3645(2)	24(1)
C(73B)	5343(2)	-1739(3)	3704(2)	27(1)
C(74B)	5743(3)	-2366(3)	3704(2)	26(1)
C(75B)	6284(2)	-2180(3)	3637(2)	24(1)
C(76B)	6445(2)	-1371(3)	3585(2)	19(1)
Cl(31)	4459(1)	6173(1)	4141(1)	56(1)
Cl(32)	3710(1)	6780(1)	3198(1)	90(1)
Cl(41)	5289(1)	5521(1)	3229(1)	47(1)
Cl(42)	5613(1)	5420(1)	2252(1)	59(1)

Cl(51)	6431(1)	4134(1)	4905(1)	69(1)
Cl(52)	5765(1)	5653(1)	4935(1)	61(1)
S(1)	7399(1)	1021(2)	1318(1)	43(1)
C(1S)	7721(2)	386(2)	978(1)	53(1)
F(1)	7950(2)	-315(2)	1243(2)	64(1)
F(2)	8172(2)	798(3)	834(2)	85(2)
F(3)	7331(2)	129(3)	511(2)	95(2)
O(1)	6923(2)	605(3)	1448(2)	66(1)
O(2)	7826(2)	1181(3)	1797(2)	62(1)
O(3)	7231(2)	1740(3)	1045(2)	87(2)
S(1')	7721(2)	386(2)	978(1)	53(1)
C(1S')	7399(1)	1021(2)	1318(1)	43(1)
O(1')	7950(2)	-315(2)	1243(2)	64(1)
O(2')	8172(2)	798(3)	834(2)	85(2)
O(3')	7331(2)	129(3)	511(2)	95(2)
F(1')	6923(2)	605(3)	1448(2)	66(1)
F(2')	7826(2)	1181(3)	1797(2)	62(1)
F(3')	7231(2)	1740(3)	1045(2)	87(2)
S(2)	7908(1)	3132(1)	6145(1)	59(1)
C(2S)	8367(4)	3480(5)	5762(3)	68(2)
F(4)	8813(3)	2952(4)	5755(2)	126(2)
F(5)	8126(3)	3545(4)	5261(2)	120(2)
F(6)	8645(2)	4202(3)	5917(2)	75(1)
O(4)	7665(3)	2399(3)	5889(2)	99(2)
O(5)	7526(2)	3816(4)	6135(3)	107(2)
O(6)	8322(3)	3020(3)	6633(2)	93(2)
C(3S)	3735(3)	6357(4)	3805(2)	51(2)
C(4S)	5867(3)	5583(4)	2927(2)	44(2)
C(5S)	5825(4)	4764(5)	4597(3)	84(3)
C(6S)	5875(10)	337(16)	383(9)	126(8)
Cl(61)	5295(2)	799(5)	593(2)	152(3)
Cl(62)	5819(2)	782(4)	-265(2)	108(2)
C(6S')	5905(10)	118(14)	30(10)	98(7)
Cl(63)	5894(3)	1174(4)	215(4)	144(3)
Cl(64)	5382(4)	60(6)	-561(3)	162(3)

Table S3. Bond lengths [Å] and angles [°] for **3**.

Ru(1A)-N(1A)	2.023(4)	Ru(1A)-N(2A)	2.169(4)
Ru(1A)-P(1A)	2.2837(14)	Ru(1A)-P(3A)	2.2980(15)
Ru(1A)-P(2A)	2.3383(14)	P(1A)-C(31A)	1.825(5)
P(1A)-C(12A)	1.838(5)	P(1A)-C(21A)	1.839(5)
P(2A)-C(51A)	1.827(5)	P(2A)-C(14A)	1.833(5)
P(2A)-C(41A)	1.836(5)	P(3A)-C(61A)	1.825(5)
P(3A)-C(71A)	1.837(5)	P(3A)-C(16A)	1.850(5)
N(1A)-C(1A)	1.121(6)	N(2A)-C(11A)	1.498(6)
N(2A)-C(15A)	1.503(6)	N(2A)-C(13A)	1.508(6)
C(1A)-C(2A)	1.460(7)	C(11A)-C(12A)	1.526(7)
C(13A)-C(14A)	1.515(7)	C(15A)-C(16A)	1.516(7)
C(21A)-C(22A)	1.375(7)	C(21A)-C(26A)	1.387(7)
C(22A)-C(23A)	1.397(7)	C(23A)-C(24A)	1.357(7)
C(24A)-C(25A)	1.391(7)	C(25A)-C(26A)	1.370(7)
C(31A)-C(32A)	1.380(7)	C(31A)-C(36A)	1.398(7)
C(32A)-C(33A)	1.381(7)	C(33A)-C(34A)	1.371(7)
C(34A)-C(35A)	1.377(7)	C(35A)-C(36A)	1.379(7)
C(41A)-C(42A)	1.386(7)	C(41A)-C(46A)	1.403(7)
C(42A)-C(43A)	1.374(7)	C(43A)-C(44A)	1.383(7)
C(44A)-C(45A)	1.382(7)	C(45A)-C(46A)	1.376(7)
C(51A)-C(52A)	1.378(7)	C(51A)-C(56A)	1.389(7)
C(52A)-C(53A)	1.377(7)	C(53A)-C(54A)	1.373(8)
C(54A)-C(55A)	1.382(8)	C(55A)-C(56A)	1.376(7)
C(61A)-C(66A)	1.384(7)	C(61A)-C(62A)	1.395(7)
C(62A)-C(63A)	1.385(7)	C(63A)-C(64A)	1.391(8)
C(64A)-C(65A)	1.373(8)	C(65A)-C(66A)	1.385(7)
C(71A)-C(76A)	1.384(7)	C(71A)-C(72A)	1.396(7)
C(72A)-C(73A)	1.384(8)	C(73A)-C(74A)	1.351(8)
C(74A)-C(75A)	1.383(8)	C(75A)-C(76A)	1.391(7)
Ru(1B)-N(1B)	2.024(4)	Ru(1B)-N(2B)	2.167(4)
Ru(1B)-P(1B)	2.2963(14)	Ru(1B)-P(3B)	2.3007(14)
Ru(1B)-P(2B)	2.3289(14)	P(1B)-C(31B)	1.836(5)
P(1B)-C(21B)	1.839(5)	P(2B)-C(41B)	1.820(5)
P(2B)-C(14B)	1.835(5)	P(2B)-C(51B)	1.839(5)

P(3B)-C(61B)	1.812(5)	P(3B)-C(16B)	1.826(5)
P(3B)-C(71B)	1.827(5)	N(1B)-C(1B)	1.131(6)
N(2B)-C(11B)	1.507(6)	N(2B)-C(15B)	1.514(6)
N(2B)-C(13B)	1.515(6)	C(1B)-C(2B)	1.470(7)
C(11B)-C(12B)	1.505(7)	C(13B)-C(14B)	1.511(7)
C(15B)-C(16B)	1.500(7)	C(21B)-C(22B)	1.365(7)
C(21B)-C(26B)	1.395(7)	C(22B)-C(23B)	1.390(7)
C(23B)-C(24B)	1.383(8)	C(24B)-C(25B)	1.377(8)
C(25B)-C(26B)	1.385(7)	C(31B)-C(36B)	1.383(7)
C(31B)-C(32B)	1.402(7)	C(32B)-C(33B)	1.386(7)
C(33B)-C(34B)	1.356(8)	C(34B)-C(35B)	1.357(8)
C(35B)-C(36B)	1.390(8)	C(41B)-C(42B)	1.393(7)
C(41B)-C(46B)	1.393(7)	C(42B)-C(43B)	1.386(7)
C(43B)-C(44B)	1.362(8)	C(44B)-C(45B)	1.368(8)
C(45B)-C(46B)	1.383(7)	C(51B)-C(52B)	1.380(7)
C(51B)-C(56B)	1.402(7)	C(52B)-C(53B)	1.371(7)
C(53B)-C(54B)	1.366(8)	C(54B)-C(55B)	1.375(8)
C(55B)-C(56B)	1.389(7)	C(61B)-C(62B)	1.384(7)
C(61B)-C(66B)	1.410(7)	C(62B)-C(63B)	1.388(7)
C(63B)-C(64B)	1.374(8)	C(64B)-C(65B)	1.369(8)
C(65B)-C(66B)	1.374(7)	C(71B)-C(72B)	1.391(7)
C(71B)-C(76B)	1.402(7)	C(72B)-C(73B)	1.392(7)
C(73B)-C(74B)	1.379(7)	C(74B)-C(75B)	1.367(7)
C(75B)-C(76B)	1.368(7)	Cl(31)-C(3S)	1.738(7)
Cl(32)-C(3S)	1.741(7)	Cl(41)-C(4S)	1.757(6)
Cl(42)-C(4S)	1.764(6)	Cl(51)-C(5S)	1.772(8)
Cl(52)-C(5S)	1.711(8)	S(1)-O(3)	1.367(5)
S(1)-O(1)	1.423(5)	S(1)-O(2)	1.432(5)
S(1)-C(1S)	1.670(4)	C(1S)-F(1)	1.362(5)
C(1S)-F(2)	1.386(5)	C(1S)-F(3)	1.407(5)
S(2)-O(4)	1.406(5)	S(2)-O(5)	1.415(6)
S(2)-O(6)	1.422(5)	S(2)-C(2S)	1.759(9)
C(2S)-F(5)	1.314(8)	C(2S)-F(6)	1.342(8)
C(2S)-F(4)	1.355(9)	C(6S)-Cl(61)	1.77(2)
C(6S)-Cl(62)	1.84(2)	C(6S')-Cl(64)	1.74(2)
C(6S')-Cl(63)	1.76(2)		

N(1A)-Ru(1A)-N(2A)	178.19(16)	N(1A)-Ru(1A)-P(1A)	96.35(12)
N(2A)-Ru(1A)-P(1A)	84.41(11)	N(1A)-Ru(1A)-P(3A)	94.67(12)
N(2A)-Ru(1A)-P(3A)	83.88(11)	P(1A)-Ru(1A)-P(3A)	149.34(5)
N(1A)-Ru(1A)-P(2A)	97.35(12)	N(2A)-Ru(1A)-P(2A)	84.07(10)
P(1A)-Ru(1A)-P(2A)	102.70(5)	P(3A)-Ru(1A)-P(2A)	104.13(5)
C(31A)-P(1A)-C(12A)	105.0(2)	C(31A)-P(1A)-C(21A)	99.7(2)
C(12A)-P(1A)-C(21A)	104.5(2)	C(31A)-P(1A)-Ru(1A)	126.44(16)
C(12A)-P(1A)-Ru(1A)	98.94(17)	C(21A)-P(1A)-Ru(1A)	119.73(17)
C(51A)-P(2A)-C(14A)	105.1(2)	C(51A)-P(2A)-C(41A)	98.8(2)
C(14A)-P(2A)-C(41A)	104.5(2)	C(51A)-P(2A)-Ru(1A)	122.14(17)
C(14A)-P(2A)-Ru(1A)	100.79(17)	C(41A)-P(2A)-Ru(1A)	123.26(17)
C(61A)-P(3A)-C(71A)	99.8(2)	C(61A)-P(3A)-C(16A)	104.2(2)
C(71A)-P(3A)-C(16A)	103.3(2)	C(61A)-P(3A)-Ru(1A)	126.03(16)
C(71A)-P(3A)-Ru(1A)	117.97(18)	C(16A)-P(3A)-Ru(1A)	102.81(18)
C(1A)-N(1A)-Ru(1A)	175.6(4)	C(11A)-N(2A)-C(15A)	107.7(4)
C(11A)-N(2A)-C(13A)	106.2(4)	C(15A)-N(2A)-C(13A)	108.2(4)
C(11A)-N(2A)-Ru(1A)	113.9(3)	C(15A)-N(2A)-Ru(1A)	109.1(3)
C(13A)-N(2A)-Ru(1A)	111.6(3)	N(1A)-C(1A)-C(2A)	177.9(6)
N(2A)-C(11A)-C(12A)	112.0(4)	C(11A)-C(12A)-P(1A)	106.9(3)
N(2A)-C(13A)-C(14A)	111.7(4)	C(13A)-C(14A)-P(2A)	107.7(3)
N(2A)-C(15A)-C(16A)	113.3(4)	C(15A)-C(16A)-P(3A)	109.7(3)
C(22A)-C(21A)-C(26A)	118.4(5)	C(22A)-C(21A)-P(1A)	120.6(4)
C(26A)-C(21A)-P(1A)	121.0(4)	C(21A)-C(22A)-C(23A)	121.1(5)
C(24A)-C(23A)-C(22A)	119.7(5)	C(23A)-C(24A)-C(25A)	119.7(5)
C(26A)-C(25A)-C(24A)	120.5(5)	C(25A)-C(26A)-C(21A)	120.5(5)
C(32A)-C(31A)-C(36A)	118.2(5)	C(32A)-C(31A)-P(1A)	125.5(4)
C(36A)-C(31A)-P(1A)	116.3(4)	C(31A)-C(32A)-C(33A)	119.8(5)
C(34A)-C(33A)-C(32A)	121.7(5)	C(33A)-C(34A)-C(35A)	119.1(5)
C(34A)-C(35A)-C(36A)	119.8(5)	C(35A)-C(36A)-C(31A)	121.3(5)
C(42A)-C(41A)-C(46A)	117.9(5)	C(42A)-C(41A)-P(2A)	123.7(4)
C(46A)-C(41A)-P(2A)	118.4(4)	C(43A)-C(42A)-C(41A)	121.0(5)
C(42A)-C(43A)-C(44A)	120.8(5)	C(45A)-C(44A)-C(43A)	119.0(5)
C(46A)-C(45A)-C(44A)	120.4(5)	C(45A)-C(46A)-C(41A)	120.9(5)
C(52A)-C(51A)-C(56A)	118.4(5)	C(52A)-C(51A)-P(2A)	123.7(4)
C(56A)-C(51A)-P(2A)	117.7(4)	C(53A)-C(52A)-C(51A)	120.6(5)

C(54A)-C(53A)-C(52A)	120.3(5)	C(53A)-C(54A)-C(55A)	120.0(5)
C(56A)-C(55A)-C(54A)	119.2(5)	C(55A)-C(56A)-C(51A)	121.3(5)
C(66A)-C(61A)-C(62A)	118.0(5)	C(66A)-C(61A)-P(3A)	119.6(4)
C(62A)-C(61A)-P(3A)	122.1(4)	C(63A)-C(62A)-C(61A)	121.2(5)
C(62A)-C(63A)-C(64A)	119.4(6)	C(65A)-C(64A)-C(63A)	120.0(6)
C(64A)-C(65A)-C(66A)	120.1(6)	C(61A)-C(66A)-C(65A)	121.3(6)
C(76A)-C(71A)-C(72A)	119.0(5)	C(76A)-C(71A)-P(3A)	122.0(4)
C(72A)-C(71A)-P(3A)	119.0(4)	C(73A)-C(72A)-C(71A)	119.6(5)
C(74A)-C(73A)-C(72A)	121.5(6)	C(73A)-C(74A)-C(75A)	119.7(6)
C(74A)-C(75A)-C(76A)	120.1(6)	C(71A)-C(76A)-C(75A)	120.2(5)
N(1B)-Ru(1B)-N(2B)	175.65(15)	N(1B)-Ru(1B)-P(1B)	94.23(12)
N(2B)-Ru(1B)-P(1B)	83.76(11)	N(1B)-Ru(1B)-P(3B)	96.42(12)
N(2B)-Ru(1B)-P(3B)	84.34(11)	P(1B)-Ru(1B)-P(3B)	159.20(5)
N(1B)-Ru(1B)-P(2B)	99.51(11)	N(2B)-Ru(1B)-P(2B)	84.55(11)
P(1B)-Ru(1B)-P(2B)	95.60(5)	P(3B)-Ru(1B)-P(2B)	100.19(5)
C(31B)-P(1B)-C(12B)	102.8(2)	C(31B)-P(1B)-C(21B)	99.5(2)
C(12B)-P(1B)-C(21B)	107.9(2)	C(31B)-P(1B)-Ru(1B)	124.89(17)
C(12B)-P(1B)-Ru(1B)	102.33(17)	C(21B)-P(1B)-Ru(1B)	117.78(18)
C(41B)-P(2B)-C(14B)	104.7(2)	C(41B)-P(2B)-C(51B)	100.0(2)
C(14B)-P(2B)-C(51B)	104.6(2)	C(41B)-P(2B)-Ru(1B)	124.18(16)
C(14B)-P(2B)-Ru(1B)	99.00(16)	C(51B)-P(2B)-Ru(1B)	121.69(16)
C(61B)-P(3B)-C(16B)	105.6(2)	C(61B)-P(3B)-C(71B)	100.0(2)
C(16B)-P(3B)-C(71B)	103.4(2)	C(61B)-P(3B)-Ru(1B)	126.32(17)
C(16B)-P(3B)-Ru(1B)	100.82(16)	C(71B)-P(3B)-Ru(1B)	118.06(17)
C(1B)-N(1B)-Ru(1B)	174.1(4)	C(11B)-N(2B)-C(15B)	104.2(4)
C(11B)-N(2B)-C(13B)	111.2(4)	C(15B)-N(2B)-C(13B)	106.0(4)
C(11B)-N(2B)-Ru(1B)	108.9(3)	C(15B)-N(2B)-Ru(1B)	111.2(3)
C(13B)-N(2B)-Ru(1B)	114.8(3)	N(1B)-C(1B)-C(2B)	177.4(5)
C(12B)-C(11B)-N(2B)	111.7(4)	C(11B)-C(12B)-P(1B)	110.0(4)
C(14B)-C(13B)-N(2B)	114.7(4)	C(13B)-C(14B)-P(2B)	110.3(3)
C(16B)-C(15B)-N(2B)	111.1(4)	C(15B)-C(16B)-P(3B)	107.3(3)
C(22B)-C(21B)-C(26B)	119.0(5)	C(22B)-C(21B)-P(1B)	121.4(4)
C(26B)-C(21B)-P(1B)	119.6(4)	C(21B)-C(22B)-C(23B)	121.2(5)
C(24B)-C(23B)-C(22B)	119.5(6)	C(25B)-C(24B)-C(23B)	119.8(5)
C(24B)-C(25B)-C(26B)	120.2(5)	C(25B)-C(26B)-C(21B)	120.2(5)
C(36B)-C(31B)-C(32B)	117.6(5)	C(36B)-C(31B)-P(1B)	125.4(4)

C(32B)-C(31B)-P(1B)	116.9(4)	C(33B)-C(32B)-C(31B)	120.8(5)
C(34B)-C(33B)-C(32B)	120.0(6)	C(33B)-C(34B)-C(35B)	120.5(6)
C(34B)-C(35B)-C(36B)	120.5(6)	C(31B)-C(36B)-C(35B)	120.5(5)
C(42B)-C(41B)-C(46B)	117.7(5)	C(42B)-C(41B)-P(2B)	123.3(4)
C(46B)-C(41B)-P(2B)	118.9(4)	C(43B)-C(42B)-C(41B)	121.0(5)
C(44B)-C(43B)-C(42B)	120.0(5)	C(43B)-C(44B)-C(45B)	120.4(5)
C(44B)-C(45B)-C(46B)	120.3(5)	C(45B)-C(46B)-C(41B)	120.6(5)
C(52B)-C(51B)-C(56B)	118.9(5)	C(52B)-C(51B)-P(2B)	124.2(4)
C(56B)-C(51B)-P(2B)	116.9(4)	C(53B)-C(52B)-C(51B)	121.4(5)
C(54B)-C(53B)-C(52B)	119.6(6)	C(53B)-C(54B)-C(55B)	120.6(5)
C(54B)-C(55B)-C(56B)	120.3(5)	C(55B)-C(56B)-C(51B)	119.1(5)
C(62B)-C(61B)-C(66B)	117.9(5)	C(62B)-C(61B)-P(3B)	123.9(4)
C(66B)-C(61B)-P(3B)	118.2(4)	C(61B)-C(62B)-C(63B)	121.6(5)
C(64B)-C(63B)-C(62B)	118.9(5)	C(65B)-C(64B)-C(63B)	120.8(5)
C(64B)-C(65B)-C(66B)	120.6(6)	C(65B)-C(66B)-C(61B)	120.1(5)
C(72B)-C(71B)-C(76B)	117.6(5)	C(72B)-C(71B)-P(3B)	122.1(4)
C(76B)-C(71B)-P(3B)	120.3(4)	C(71B)-C(72B)-C(73B)	121.2(5)
C(74B)-C(73B)-C(72B)	119.4(5)	C(75B)-C(74B)-C(73B)	120.1(5)
C(74B)-C(75B)-C(76B)	120.9(5)	C(75B)-C(76B)-C(71B)	120.8(5)
O(3)-S(1)-O(1)	112.7(4)	O(3)-S(1)-O(2)	111.4(3)
O(1)-S(1)-O(2)	106.5(3)	O(3)-S(1)-C(1S)	109.6(3)
O(1)-S(1)-C(1S)	110.2(3)	O(2)-S(1)-C(1S)	106.2(3)
F(1)-C(1S)-F(2)	107.8(4)	F(1)-C(1S)-F(3)	107.4(3)
F(2)-C(1S)-F(3)	105.7(4)	F(1)-C(1S)-S(1)	113.4(3)
F(2)-C(1S)-S(1)	110.3(3)	F(3)-C(1S)-S(1)	111.9(3)
O(4)-S(2)-O(5)	117.3(4)	O(4)-S(2)-O(6)	115.9(4)
O(5)-S(2)-O(6)	113.6(4)	O(4)-S(2)-C(2S)	102.6(4)
O(5)-S(2)-C(2S)	103.1(4)	O(6)-S(2)-C(2S)	101.0(4)
F(5)-C(2S)-F(6)	107.2(7)	F(5)-C(2S)-F(4)	99.9(7)
F(6)-C(2S)-F(4)	102.9(7)	F(5)-C(2S)-S(2)	116.4(6)
F(6)-C(2S)-S(2)	114.8(5)	F(4)-C(2S)-S(2)	113.8(6)
Cl(31)-C(3S)-Cl(32)	109.9(4)	Cl(41)-C(4S)-Cl(42)	111.0(3)
Cl(52)-C(5S)-Cl(51)	113.3(4)	Cl(61)-C(6S)-Cl(62)	105.0(12)
Cl(64)-C(6S')-Cl(63)	104.3(13)		

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1A)	19(1)	15(1)	13(1)	1(1)	4(1)	0(1)
P(1A)	20(1)	18(1)	16(1)	1(1)	3(1)	2(1)
P(2A)	19(1)	17(1)	15(1)	2(1)	5(1)	1(1)
P(3A)	21(1)	24(1)	19(1)	4(1)	7(1)	-1(1)
N(1A)	18(2)	20(2)	19(2)	4(2)	4(2)	2(2)
N(2A)	23(2)	14(2)	14(2)	2(2)	6(2)	3(2)
C(1A)	26(3)	26(3)	20(3)	-4(2)	3(2)	4(2)
C(2A)	45(4)	38(4)	37(3)	-21(3)	8(3)	6(3)
C(11A)	31(3)	23(3)	15(2)	-2(2)	2(2)	-1(2)
C(12A)	21(3)	22(3)	16(2)	3(2)	2(2)	1(2)
C(13A)	33(3)	21(3)	17(3)	-3(2)	6(2)	2(2)
C(14A)	24(3)	25(3)	21(3)	-1(2)	4(2)	2(2)
C(15A)	25(3)	30(3)	19(3)	2(2)	11(2)	-3(2)
C(16A)	32(3)	27(3)	20(3)	4(2)	11(2)	-1(2)
C(21A)	32(3)	16(3)	15(2)	2(2)	10(2)	4(2)
C(22A)	25(3)	24(3)	19(3)	-1(2)	9(2)	3(2)
C(23A)	32(3)	26(3)	28(3)	-6(2)	13(3)	-5(3)
C(24A)	39(4)	19(3)	30(3)	2(2)	15(3)	6(3)
C(25A)	29(3)	22(3)	30(3)	-3(2)	8(3)	4(3)
C(26A)	26(3)	27(3)	24(3)	4(2)	5(2)	5(2)
C(31A)	23(3)	19(3)	23(3)	0(2)	6(2)	9(2)
C(32A)	28(3)	31(3)	24(3)	1(2)	5(3)	0(3)
C(33A)	21(3)	35(3)	38(3)	-5(3)	-2(3)	-5(3)
C(34A)	25(3)	28(3)	48(4)	-2(3)	18(3)	-3(3)
C(35A)	37(4)	23(3)	32(3)	0(2)	15(3)	10(3)
C(36A)	21(3)	15(3)	28(3)	-2(2)	5(2)	3(2)
C(41A)	22(3)	21(3)	21(3)	7(2)	3(2)	3(2)
C(42A)	24(3)	24(3)	23(3)	1(2)	7(2)	0(2)
C(43A)	20(3)	27(3)	33(3)	2(3)	3(2)	-5(2)
C(44A)	24(3)	35(3)	35(3)	10(3)	12(3)	3(3)
C(45A)	39(4)	28(3)	24(3)	4(2)	16(3)	4(3)

C(46A)	25(3)	25(3)	20(3)	2(2)	2(2)	0(2)
C(51A)	16(3)	21(3)	20(3)	4(2)	5(2)	0(2)
C(52A)	25(3)	26(3)	29(3)	0(2)	-2(3)	5(2)
C(53A)	35(4)	17(3)	54(4)	-4(3)	2(3)	7(3)
C(54A)	23(3)	31(3)	39(3)	14(3)	-3(3)	2(3)
C(55A)	24(3)	41(4)	15(3)	8(2)	1(2)	0(3)
C(56A)	25(3)	21(3)	24(3)	1(2)	9(2)	4(2)
C(61A)	17(3)	26(3)	31(3)	10(2)	8(2)	-7(2)
C(62A)	19(3)	36(3)	29(3)	10(3)	8(2)	0(3)
C(63A)	34(4)	39(4)	51(4)	17(3)	23(3)	11(3)
C(64A)	20(3)	56(4)	37(3)	24(3)	9(3)	6(3)
C(65A)	28(3)	56(4)	28(3)	17(3)	-1(3)	-12(3)
C(66A)	29(3)	32(3)	28(3)	3(3)	8(3)	-5(3)
C(71A)	21(3)	26(3)	16(2)	6(2)	1(2)	-4(2)
C(72A)	25(3)	34(3)	27(3)	4(3)	1(2)	-1(3)
C(73A)	28(4)	55(4)	30(3)	14(3)	3(3)	-16(3)
C(74A)	40(4)	39(4)	28(3)	4(3)	-4(3)	-16(3)
C(75A)	52(4)	31(3)	19(3)	0(2)	4(3)	-11(3)
C(76A)	35(3)	29(3)	18(3)	8(2)	2(2)	-5(3)
Ru(1B)	15(1)	14(1)	17(1)	1(1)	5(1)	1(1)
P(1B)	17(1)	22(1)	18(1)	2(1)	4(1)	1(1)
P(2B)	17(1)	16(1)	19(1)	0(1)	6(1)	0(1)
P(3B)	17(1)	14(1)	24(1)	-1(1)	7(1)	1(1)
N(1B)	17(2)	19(2)	15(2)	4(2)	6(2)	1(2)
N(2B)	21(2)	22(2)	16(2)	1(2)	5(2)	-1(2)
C(1B)	16(3)	18(3)	19(3)	4(2)	4(2)	-5(2)
C(2B)	32(3)	37(3)	31(3)	-13(3)	15(3)	-3(3)
C(11B)	24(3)	36(3)	26(3)	2(3)	11(2)	3(3)
C(12B)	19(3)	39(3)	18(3)	3(2)	3(2)	-2(2)
C(13B)	32(3)	18(3)	23(3)	-7(2)	14(2)	-6(2)
C(14B)	23(3)	19(3)	26(3)	-3(2)	8(2)	-5(2)
C(15B)	23(3)	15(3)	25(3)	3(2)	14(2)	0(2)
C(16B)	13(3)	24(3)	35(3)	-4(2)	10(2)	-5(2)
C(21B)	19(3)	27(3)	23(3)	12(2)	7(2)	3(2)
C(22B)	24(3)	26(3)	27(3)	8(2)	10(2)	7(2)
C(23B)	37(4)	35(4)	30(3)	5(3)	10(3)	1(3)

C(24B)	22(3)	39(4)	41(3)	21(3)	15(3)	13(3)
C(25B)	16(3)	36(3)	41(3)	19(3)	5(3)	1(3)
C(26B)	24(3)	33(3)	29(3)	13(3)	8(3)	-5(3)
C(31B)	9(3)	24(3)	34(3)	2(2)	0(2)	2(2)
C(32B)	18(3)	27(3)	36(3)	7(3)	5(3)	6(2)
C(33B)	26(3)	35(4)	43(4)	12(3)	13(3)	8(3)
C(34B)	23(3)	43(4)	56(4)	23(3)	11(3)	6(3)
C(35B)	19(3)	25(3)	54(4)	5(3)	-3(3)	2(3)
C(36B)	23(3)	32(3)	36(3)	2(3)	6(3)	7(3)
C(41B)	15(3)	25(3)	22(3)	11(2)	6(2)	6(2)
C(42B)	16(3)	25(3)	32(3)	3(2)	4(2)	4(2)
C(43B)	21(3)	31(3)	41(3)	9(3)	9(3)	-3(3)
C(44B)	24(3)	37(4)	54(4)	24(3)	22(3)	4(3)
C(45B)	38(4)	32(3)	34(3)	6(3)	28(3)	10(3)
C(46B)	30(3)	25(3)	31(3)	3(3)	10(3)	1(3)
C(51B)	20(3)	14(3)	30(3)	10(2)	4(2)	1(2)
C(52B)	26(3)	21(3)	38(3)	8(3)	6(3)	2(2)
C(53B)	23(3)	27(3)	48(4)	2(3)	7(3)	3(2)
C(54B)	24(3)	29(3)	54(4)	16(3)	1(3)	-2(3)
C(55B)	35(4)	39(4)	31(3)	13(3)	2(3)	-11(3)
C(56B)	23(3)	29(3)	30(3)	8(3)	7(3)	-2(2)
C(61B)	16(3)	14(3)	32(3)	1(2)	-1(2)	2(2)
C(62B)	24(3)	23(3)	38(3)	8(3)	8(3)	-1(2)
C(63B)	19(3)	21(3)	54(4)	8(3)	-4(3)	3(2)
C(64B)	35(4)	29(3)	39(4)	-3(3)	-13(3)	-1(3)
C(65B)	46(4)	30(3)	30(3)	-2(3)	9(3)	5(3)
C(66B)	31(3)	18(3)	29(3)	-4(2)	-5(3)	8(2)
C(71B)	25(3)	19(3)	13(2)	1(2)	6(2)	2(2)
C(72B)	14(3)	31(3)	24(3)	-7(2)	2(2)	-3(2)
C(73B)	30(3)	30(3)	22(3)	-7(2)	8(2)	-10(3)
C(74B)	47(4)	14(3)	16(3)	-4(2)	5(3)	-4(3)
C(75B)	34(3)	21(3)	15(3)	-4(2)	4(2)	5(2)
C(76B)	21(3)	21(3)	16(3)	-3(2)	5(2)	-3(2)
Cl(31)	52(1)	70(1)	45(1)	-13(1)	11(1)	4(1)
Cl(32)	126(2)	65(1)	58(1)	25(1)	-16(1)	-36(1)
Cl(41)	51(1)	36(1)	64(1)	-4(1)	32(1)	-5(1)

Cl(42)	82(1)	52(1)	44(1)	7(1)	17(1)	22(1)
Cl(51)	80(2)	61(1)	73(1)	20(1)	31(1)	24(1)
Cl(52)	48(1)	47(1)	77(1)	-8(1)	-5(1)	-2(1)
S(1)	37(1)	39(1)	49(1)	17(1)	3(1)	-3(1)
C(1S)	45(2)	46(2)	60(2)	15(2)	-2(2)	-7(2)
F(1)	77(3)	41(2)	68(3)	8(2)	9(2)	1(2)
F(2)	76(3)	103(4)	80(3)	16(3)	25(3)	-28(3)
F(3)	135(5)	84(4)	53(3)	-10(2)	2(3)	-25(3)
O(1)	44(3)	65(3)	92(4)	19(3)	25(3)	2(3)
O(2)	79(4)	46(3)	51(3)	-8(2)	-1(3)	6(3)
O(3)	78(4)	40(3)	123(5)	20(3)	-12(4)	8(3)
S(1')	45(2)	46(2)	60(2)	15(2)	-2(2)	-7(2)
C(1S')	37(1)	39(1)	49(1)	17(1)	3(1)	-3(1)
O(1')	77(3)	41(2)	68(3)	8(2)	9(2)	1(2)
O(2')	76(3)	103(4)	80(3)	16(3)	25(3)	-28(3)
O(3')	135(5)	84(4)	53(3)	-10(2)	2(3)	-25(3)
F(1')	44(3)	65(3)	92(4)	19(3)	25(3)	2(3)
F(2')	79(4)	46(3)	51(3)	-8(2)	-1(3)	6(3)
F(3')	78(4)	40(3)	123(5)	20(3)	-12(4)	8(3)
S(2)	81(2)	36(1)	52(1)	-4(1)	2(1)	-8(1)
C(2S)	91(7)	42(5)	58(5)	-30(4)	-5(5)	3(4)
F(4)	150(6)	101(4)	133(5)	-39(4)	50(4)	28(4)
F(5)	185(6)	119(5)	42(3)	-15(3)	6(3)	-58(4)
F(6)	79(3)	71(3)	75(3)	-26(2)	24(3)	-18(2)
O(4)	137(6)	63(4)	84(4)	-18(3)	5(4)	-51(4)
O(5)	55(4)	67(4)	198(7)	-30(4)	30(4)	-9(3)
O(6)	135(5)	71(4)	50(3)	4(3)	-18(3)	-19(4)
C(3S)	62(5)	38(4)	42(4)	-5(3)	-8(3)	-1(3)
C(4S)	31(4)	46(4)	60(4)	3(3)	22(3)	0(3)
C(5S)	108(7)	75(6)	55(5)	-6(4)	-9(5)	33(5)
Cl(61)	96(4)	288(9)	67(3)	41(4)	16(3)	23(5)
Cl(62)	116(4)	119(4)	97(4)	23(3)	42(3)	-21(4)
Cl(63)	72(4)	82(5)	259(10)	-28(6)	6(5)	5(3)
Cl(64)	142(7)	199(9)	130(6)	-23(6)	10(5)	-10(6)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3**.

	x	y	z	U(eq)
H(1A)	2395	925	4183	19
H(2A1)	2564	-202	2517	61
H(2A2)	2485	622	2166	61
H(2A3)	1923	172	2277	61
H(11A)	3031	2381	5403	29
H(11B)	3348	2802	5002	29
H(12A)	3169	1040	5095	24
H(12B)	3794	1504	5232	24
H(13A)	2487	3612	4929	28
H(13B)	1968	3423	4423	28
H(14A)	3169	3701	4424	28
H(14B)	2635	4323	4182	28
H(15A)	2039	2360	5205	28
H(15B)	2168	1460	5000	28
H(16A)	1271	2595	4502	31
H(16B)	1189	1642	4653	31
H(22A)	2864	-111	3887	26
H(23A)	3155	-1497	3834	34
H(24A)	4122	-1872	4185	34
H(25A)	4813	-852	4553	32
H(26A)	4527	521	4598	31
H(32A)	4406	2342	5033	34
H(33A)	5253	2954	4914	40
H(34A)	5435	3020	4101	38
H(35A)	4763	2430	3391	35
H(36A)	3931	1768	3507	26
H(42A)	3606	4298	3871	28
H(43A)	4312	4670	3450	33
H(44A)	4318	4076	2651	37
H(45A)	3623	3058	2294	34

H(46A)	2920	2668	2717	29
H(52A)	2002	4775	3614	34
H(53A)	1280	5470	3001	45
H(54A)	858	4853	2205	40
H(55A)	1126	3499	2034	33
H(56A)	1818	2784	2664	27
H(62A)	976	3359	3838	33
H(63A)	260	4101	3239	47
H(64A)	-223	3473	2451	45
H(65A)	16	2121	2269	47
H(66A)	716	1374	2875	36
H(72A)	399	1015	3969	36
H(73A)	-19	-307	3909	46
H(74A)	473	-1454	3727	46
H(75A)	1391	-1296	3560	42
H(76A)	1824	25	3608	34
H(1B)	7301	-268	4073	18
H(2B1)	8317	-699	2642	48
H(2B2)	7801	-317	2189	48
H(2B3)	7703	-1178	2459	48
H(11C)	7364	1026	5294	33
H(11D)	7383	171	4989	33
H(12C)	8338	601	5257	31
H(12D)	8171	1540	5069	31
H(13C)	6587	2259	4418	28
H(13D)	7142	2249	4909	28
H(14C)	7776	2533	4417	27
H(14D)	7230	3141	4193	27
H(15C)	6465	230	4633	23
H(15D)	6300	1141	4797	23
H(16C)	5934	1514	3922	28
H(16D)	5612	675	4032	28
H(22B)	8046	-943	3887	30
H(23B)	8626	-2133	3926	41
H(24B)	9563	-2171	4494	39
H(25B)	9897	-1043	5039	38

H(26B)	9321	153	4985	34
H(32B)	8820	998	3590	32
H(33B)	9513	1947	3455	41
H(34B)	9880	2958	4065	48
H(35B)	9586	3019	4823	42
H(36B)	8893	2080	4975	37
H(42B)	8019	3550	3813	30
H(43B)	8684	4172	3416	37
H(44B)	8833	3614	2661	44
H(45B)	8371	2388	2325	37
H(46B)	7731	1725	2731	34
H(52B)	6325	3226	3741	35
H(53B)	5462	3744	3211	40
H(54B)	5233	3490	2327	45
H(55B)	5835	2654	1974	43
H(56B)	6672	2036	2513	33
H(62B)	5122	1133	3146	34
H(63B)	4529	1448	2324	40
H(64B)	4849	1104	1593	46
H(65B)	5758	503	1677	43
H(66B)	6359	201	2491	34
H(72B)	5223	-482	3641	29
H(73B)	4964	-1867	3744	32
H(74B)	5641	-2929	3751	31
H(75B)	6552	-2617	3627	28
H(76B)	6825	-1253	3544	23
H(3SA)	3552	6747	4005	61
H(3SB)	3512	5827	3762	61
H(4SA)	6167	5158	3077	53
H(4SB)	6054	6139	2992	53
H(5SA)	5862	4920	4247	101
H(5SB)	5460	4434	4552	101